THE ATOMIC WEIGHTS OF BORON AND FLUORINE

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INTRODUCTION.

When the present work was undertaken the writers contemplated the use of anhydrous borax as the initial material in determining the atomic weight of certain elements, *e.g.*, fluorine. After numerous trials, a method was worked out which admitted of the complete conversion of sodium tetraborate into sodium fluoride, and the preliminary experiments made with this method gave a value for fluorine which was practically identical with the present international figure (19.0). However, as soon as the same method was applied to borax, the purity and the anhydrous condition of which were above suspicion, the atomic weight of fluorine (on the assumption that B = 11.0) became too high.

Although it was realized from the beginning that it would be desirable to redetermine the atomic weight of boron before the latter could properly be used in fixing other atomic weights, it was not anticipated—in view of the most reliable previous work upon this constant—that it would differ much from the accepted value (11.0).

A closer study of the literature bearing upon this subject soon revealed that the inconsistencies and uncertainties in previous determinations are much greater than might reasonably be expected of a rather common, non-metallic, uniformly trivalent [1] element of low atomic weight; and thus it has come to pass that the major part of the present investigation is devoted to the determination of the atomic weight of boron. The work outlined in the following pages deals with the preparation of pure substances and the conversion, either directly or indirectly, of anhydrous sodium tetraborate into the chloride, fluoride, sulphate, nitrate, and carbonate of sodium. The atomic weight of boron was thus based upon the rather well-known atomic weights of sodium, chlorine, sulphur, nitrogen, and carbon, and (with slight variations) led to the value 10.900 for boron.

Incidentally the work also seemed to furnish sufficient data for a recalculation of the atomic weight of fluorine. The value

[1] Trivalent at least with respect to oxygen and the halogens. On the valence of boron see A. Stock, E. Kuss, and O. Priess, Ber. **47**, 3115–49 (1914).

found for boron was used in deriving the atomic weight of this element, although some calculations were referred directly to sodium sulphate, and one was based on a cross-ratio between sodium fluoride and sodium chloride. All methods, rather consistently, gave the average value 19.005 for fluorine.

Chapter III consists of a constructive, critical discussion of previous determinations based upon the analysis of borax.

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CHAPTER I. GENERAL PART.

PRINCIPLE OF THE METHOD.

According to Rosenbladt,[1] the characteristic green color imparted to an ordinary alcohol flame by boric acid was known to Geoffroy in 1732. In course of time it was found that this test became more delicate when methyl alcohol was used. In 1887 Gooch[2] and Rosenbladt,[3] both working independently, successfully adapted this qualitative test to the estimation of boric acid, which until then had presented great difficulties to the analyst.[4] In order to estimate boron in a soluble borate, for example, it was merely necessary to liberate the boric acid by the addition of a stronger acid, and then expel the former as its methyl ester, by repeated evaporations with methyl alcohol, after which the ester was hydrolyzed and the boric acid thus fixed, by a suitable absorbent or "retainer." This general method for the elimination of boric acid from borax, with certain modifications, was also pursued in the present work; the methyl borate, however, was allowed to escape, since the weights of the anhydrous borax and the residual sodium salt served to establish the desired ratios.

This volatilization method was first used in atomic weight determinations by Ramsay and Aston,[5] who distilled borax with hydrochloric acid and methyl alcohol and weighed the residual sodium chloride.

Rosenbladt expelled the boric acid in the presence of sulphuric acid. Gooch, according to his original communication, found it difficult to choose between acetic and nitric acids. As the esterification of boric acid is counteracted by water, it is readily seen that the latter should be absent, or nearly so, unless a vast excess of methyl alcohol be used. For such reasons the use of acetic

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[1] Z. anorg. Chem. **26**, 18 (1887).
[2] Chem. N. **55**, 7 (1887).
[3] Loc. cit.
[4] More recent modifications in the estimation of boric acid, and additional references, may be found in a paper by Wherry and Chapin, J. Am. Chem. Soc., **30**, 1687 (1908).
[5] J. Chem. Soc. **63**, 211 (1893).

acid seems inadvisable, since sodium acetate is not readily dehydrated. This objection does not apply to the other acids mentioned, *i.e.*, to hydrochloric, sulphuric, and nitric acids. All of these have been used in the present work. In addition carbonic acid, or rather its anhydride, has been employed in converting borax into sodium carbonate.

The action of hydrofluoric acid seems to be not strictly analogous to that of the acids just mentioned. Although sodium fluoride and boric acid are undoubtedly formed at first, a number of secondary reactions may take place between these primary products and the excess of hydrofluoric acid, leading chiefly to the formation of borofluoric acid and, possibly, of sodium borofluoride.[6] It is true that the mixture thus obtained will give up considerable portions of boric acid when evaporated with methyl alcohol, but the quantitative elimination of boric acid by this means, with reasonable quantities of methyl alcohol, seemed very doubtful. Again, sodium borofluoride, upon ignition, will give up boron trifluoride and leave sodium fluoride. However, at the temperature required to effect this decomposition, appreciable quantities of the sodium salt itself may be volatilized. At any rate, the conclusion was soon reached that the elimination of boric acid as methyl borate in the presence of an alkali fluoride and hydrofluoric acid could not be rendered sufficiently accurate for an atomic weight determination, even if it should be possible to expel boric acid completely by this method.

Therefore, if the distillation method were to be applied to borax with a view of obtaining sodium fluoride as an end-product, the problem clearly resolved itself into this: An acid had to be found which would react "normally" with borax and its sodium salt would have to be readily transposed to the fluoride by means of hydrofluoric acid. Formic acid was found to be such an acid. It gave results that left little to be desired.

Besides purity of materials, the essential prerequisites in deriving an acceptable atomic weight ratio are definite and weighable substances constituting the ratio sought and completeness of the reaction correlating the two terms of that ratio. That

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[6] See also Abegg, Fox, and Herz on possible reactions between boric acid, potassium fluoride, and hydrofluoric acid. Z. anorg. Chem. 35, 129 (1903).

borax, a well-crystallized salt of moderate solubility, represents a definite atomic aggregate seems reasonably certain. That anhydrous borax, although obtained with some difficulty, is no less definite, is practically non-hygroscopic, and may be weighed with ease, will be shown in the sequel. The other salts, namely, the chloride, fluoride, sulphate, nitrate, and carbonate of sodium, have all met with more or less application in atomic weight work. Of these the sulphate was found to be the most stable at the fusion temperature and left practically nothing to be desired when fused in a jacketed vessel. The fluoride, in spite of its high melting-point (at 980°), was somewhat volatile; but when heated in the bulb (soon to be described) could be fused to constant weight with comparative ease. Other precautions observed in the heating of these salts will be given in their appropriate places.

The completeness of the reaction, *i.e.*, the complete expulsion of boric acid, was tested for, in two cases by means of the flame spectrum; in others, with turmeric paper—by both methods with negative results. Indirectly the completeness of the reaction may be inferred from the following considerations: If a number of samples of borax had been converted, by identical operations, into only one kind of salt, *e.g.*, sodium chloride, mere concordance in the results would not necessarily prove that the elimination of boric acid had been complete; under such conditions constant errors are not unknown to have made their appearance. In the present instance, however, borax was converted into a number of different salts, involving a variety of operations and great diversity in conditions. A fair concordance obtained by the latter method would indicate that the elimination of boric acid must have been complete.

DISTILLED WATER.

Ordinary distilled water was redistilled with a little potassium permanganate made alkaline with potassium hydroxide. The first third of the distillate was rejected. The portion collected was redistilled with a little potassium bisulphate. The product was then redistilled twice. A block-tin condenser was used. The water was stored in well-seasoned flasks of resistance glass, provided with caps fitted on the outside of the neck to prevent contact of the water with ground surfaces.

The seal between the distilling flask and the metal condenser

was effected by a modification of the well-known funnel-top seal suggested by T. W. Richards. The device is shown in figure 1. The auxiliary glass bulb (*a*) is easily made from a round-bottomed flask of suitable dimensions; with accurately blown ware an excellent seal may thus be obtained without grinding. The opening at (*c*) should, of course, be in proper alignment with the constriction at (*b*), which serves as a seat for the condenser. The neck of the bulb has two side-vents (*dd*) and is loosely packed with glass wool, held in position by a clamp of platinum wire. Glass wool was used because even in careful boiling a very slight spray of the solution itself may reach this part of the apparatus.

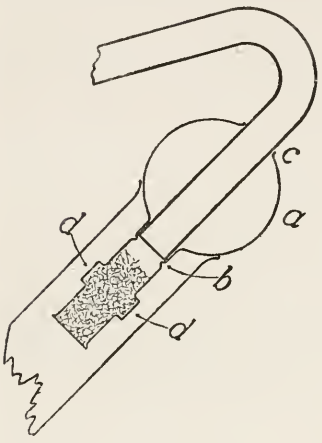

Fig. 1.

The water obtained in the preceding way was used in the recrystallizations. In the quantitative determinations small quantities of water were to be evaporated to dryness, and it was prepared by distilling once more from an all-platinum still; it was freshly prepared for each determination and stored in a platinum vessel. The "head" of the platinum still used is indicated in figure 2. The stirrup-shaped "spray-guard" (*e*) was inserted into the ground-in neck of the condenser and held in position by the pins (*f*). This still was also used for the distillation of hydrofluoric acid. In an apparatus of moderate dimensions, and particularly when the liquid is to be distilled with other dissolved or suspended substances, traces of such matter may reach the dome of the condenser, in spite of all precautions in heating. It is under such conditions that the "spray-guard" just mentioned is of value.

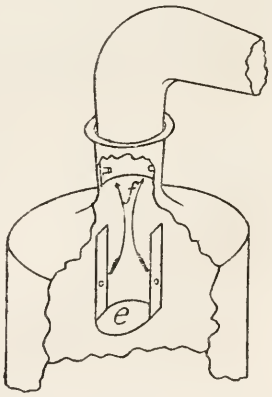

Fig. 2.

BORIC ACID.

Several courses were open for the preparation of borax. It is doubtful whether the impurities (such as silica, lime, organic matter, etc.) in commercial borax can easily be removed by recrystallization. Hence for the purposes of this investigation the synthesis of the salt from its acid and basic components in purest form, though laborious, was preferred. The further purification of the product could easily be completed by recrystallization.

Pure boric acid was prepared as follows: A good "C. P." grade was crystallized three times from water, the crystals being drained and washed centrifugally each time. The product was then dehydrated and fused to a clear glass in platinum. Approximately 500 grams of this anhydrous acid were covered with 2 liters of redistilled and almost anhydrous methyl alcohol, which contained only a trace of acetone. The mixture was boiled under a reflux condenser in an all-glass apparatus until solution was complete. In this reaction part of the boric acid forms the methyl ester, whereas the remainder probably does not react at all, or serves as a dehydrating agent and separates out on cooling in crystalline crusts on the sides of the flask. The clear liquid, containing the methyl borate, was decanted and distilled from an apparatus constructed entirely of glass. Evidently the ester was partly hydrolyzed during this process, for a considerable portion of boric acid remained in the flask.

The clear, colorless distillate, containing the methyl borate, was mixed with an equal volume of boiling water, agitated from time to time, and allowed to stand, when crystals of boric acid separated out on cooling. The product was drained and washed centrifugally and crystallized once from water. As was expected, the method gave a poor yield in the end, but the boric acid thus obtained was of great purity.

SODIUM CARBONATE.

A very pure commercial grade of sodium carbonate was fused in a platinum dish in portions of 100 grams each with a small quantity of pure, precipitated calcium carbonate.[7] After disintegration of the melt in water the cold liquid was decanted and

[7] Smith and Exner, Proc. Am. Philos. Soc. 43, No. 176, p. 134 (1904).

filtered. "Quantitative" paper and a platinum funnel were used. The paper had been specially washed with hydrochloric and hydrofluoric acids, followed by large quantities of water; finally it was treated with a hot solution of sodium carbonate before the main solution was filtered.

Traces of calcium carbonate which may contaminate the filtrate were effectively removed by a subsequent operation, consisting in the exposure of the solution of the sodium carbonate (contained in a large platinum-lined dish) to an atmosphere of

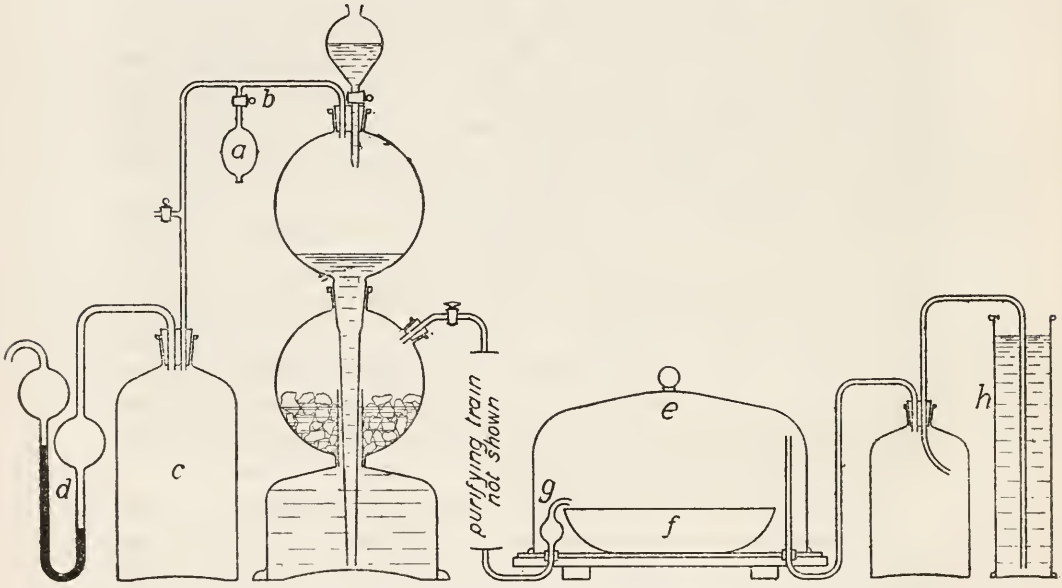

FIG. 3.

carbon dioxide for many days. The resulting sodium bicarbonate was then drained and washed centrifugally and the precipitation as bicarbonate repeated three times. Needless to say, platinum utensils were used throughout. Finally the salt was gently ignited to the normal carbonate. Spectroscopic tests showed the preparation to be free from calcium.

Figure 3, in vertical projection, shows the apparatus used in precipitating the bicarbonate. The arrangement was found quite convenient for conducting the precipitation under pressure and practically without interruption. The air in the upper reservoir

of the Kipp generator is compressed by means of the stout rubber bulb (*a*) and the stop-cock (*b*) closed. The empty bottle (*c*) merely serves as a reservoir for the compressed air and communicates with the mercury manometer (*d*), which also serves as a safety valve. The bell-jar (*e*) is ground upon a glass plate and covers the platinum dish (*f*) containing the sodium carbonate solution. After the bell-jar has been filled with carbon dioxide through the delivery tube (*g*) (which does not come in contact with the solution) cylinder (*h*) may be filled with water to the desired height. In the present instance an additional pressure of only about 30 cm. of water was applied. This pressure, of course, does not hasten the absorption of the gas very markedly, but as the reaction was quite slow a slight acceleration was not unwelcome. Even under the pressure applied, the upper reservoir of the generator had to be wired to its base and the bell-jar securely clamped to the plate. As practically no carbon dioxide is wasted, the apparatus (when properly adjusted) will run for days and requires little attention; it is advisable, of course, to restore the original pressure occasionally by means of the rubber bulb.

The carbon dioxide was generated by the action of pure hydrochloric acid on white marble. The gas passed through two large towers; the first contained beads coated with moist sodium bicarbonate, the other was similarly charged with moist silver carbonate. Finally, before reaching the bell-jar, it was conducted through two wash-bottles containing solutions of sodium bicarbonate. The contents of the platinum dish remained entirely free from chloride.

BORAX.

Crystallized boric acid and sodium carbonate, prepared as indicated in the preceding sections, were next brought together by introducing small portions of the acid in solid form into a boiling solution of the carbonate contained in a platinum dish, until the boric acid was slightly in excess of the theoretical requirement for the formation of the tetraborate. Boiling of the clear solution was continued until no more carbon dioxide was evolved. The crystal meal, which separated out on cooling and stirring, was drained on the platinum cones of a hand centrifugal and

washed with a small quantity of cold water, previously boiled. The product was recrystallized twice from water free from carbon dioxide and drained and washed as before. In these recrystallizations the solution was "inoculated" with a trace of the decahydrate (prepared for the purpose) as soon as the temperature of the solution had fallen a little below 55°, which approximately marks the transition point between the penta- and decahydrates. The preparation thus obtained was used in some of the preliminary determinations.

There seemed to be a remote possibility that this borax was not entirely free from unknown organic derivatives which might have accompanied the boric acid because of its preparation from the methyl ester. While no evidence to this effect could be obtained, it seemed best to dehydrate the borax and fuse it to a clear glass before the final recrystallizations. Pure borax from another source had been fused for hours in the platinum dish before it was used for the fusion of the borax in question. Even at the risk of making a rather superfluous statement, mention must be made of the extreme brilliancy of the "borax glass" thus obtained and the total absence of the slightest color from the melt, even when examined "end-on" and in thick layers.

The "borax glass" was dissolved in water, free from carbon dioxide, and recrystallized four times in the manner and with the precautions already indicated. The product was dried and partly dehydrated over solid potassium hydroxide. The salt, even before the final recrystallizations, contained no perceptible traces of carbonate, for a powdered sample moistened with water and dilute hydrochloric acid remained free from bubbles, even when examined under the magnifying glass. Under the microscope the crystals presented an entirely uniform and homogeneous appearance. In some instances the mother liquors were allowed to evaporate to dryness over caustic potash, when nothing but borax (free from carbonate) was obtained. The crystals obtained by spontaneous evaporation of such solutions were remarkably stable and showed no sign of efflorescence, even when exposed for weeks to ordinary atmospheric conditions.

Reliable tests indicating the presence, in borax, of traces of other borates (either more basic or more acid in character) are

lacking. However, such borates are prepared only with difficulty and as, in the present instance, the proportion of the components and the conditions of formation were those corresponding to the tetraborate with 10 molecules of water, it may safely be assumed that the preparation was "pure" also from this point of view. The final product was used in the experiments recorded in table 1.

METHYL ALCOHOL.

The methyl alcohol used in the quantitative elimination of boric acid from borax should, of course, be anhydrous, or very nearly so. It should also be as pure as possible, for it seems that the smaller the amount of the usual impurities in the alcohol, the more readily will methyl borate be formed with a minimum expenditure of the reagent. The methyl alcohol for the final determinations, therefore, was prepared by the saponification of methyl oxalate which admittedly yields a very pure product.

The methyl oxalate was made from dehydrated oxalic acid and a good grade of almost anhydrous commercial methyl alcohol. The mixture was heated in the water-bath for several hours under a reflux condenser. It was then distilled from an all-glass apparatus and the distillate collected as soon as it began to solidify in the receiver. The product was drained and washed centrifugally. Almost 2 kilograms of methyl oxalate were obtained in this manner. It was melted on the water-bath and, after the addition of some water, saponified by introducing small quantities of caustic soda solution through the upright condenser until an excess of the alkali had been added. The resulting mixture was boiled for several hours under the reflux condenser and finally distilled.

In testing the purity of the resulting aqueous methyl alcohol, it was found that a neutral solution of silver nitrate produced a slight white precipitate. The latter dissolved readily in dilute nitric acid and did not consist of silver carbonate. The addition of silver nitrate to extremely dilute solutions of ammonium hydroxide and other soluble hydroxides gave similar precipitates, which turned brown on boiling. The test seemed to indicate, therefore, that the methyl alcohol was contaminated with a trace of some volatile base, such as ammonia, and that the precipitate

consisted of silver hydroxide.[8] That traces of sodium hydroxide should have been carried into the receiver seemed unlikely, for special precautions were observed in the distillation. Ammonia, however, might have been introduced from the caustic soda, which may contain (and was found to contain) traces of this substance. The silver nitrate test seemed extremely delicate. It will be recalled that Nessler's test can not be applied in the presence of alcohol, and indicators (with the possible exception of methyl orange) did not show any perceptible alkalinity of the alcohol.

The trace of free ammonia, though probably unobjectionable in the present case, was removed in the following manner: An aliquot portion of the methyl alcohol was diluted with more water and mixed with a few drops of very dilute hydrochloric acid until methyl orange, the indicator, showed a slight acidity. The main portion of the alcohol was then mixed with the required amount of the same acid and distilled; a considerable portion, however, was allowed to remain behind and was rejected. The distillate was boiled for a long time, under a reflux condenser, with sodium hydroxide prepared from sodium and, after distillation, gave no test with silver nitrate. The process was then repeated twice. Finally the alcohol (distilled again from pure sodium hydroxide) was fractionated with a Hempel column, boiled with lime for several days, and distilled. The resulting product still contained almost 1 per cent. of water, as indicated by the hydrometer. As the residues, to be treated with the alcohol in the quantitative determinations, were never absolutely anhydrous, it did not seem worth while to remove the last fraction of water from the alcohol by other means.

[8] Silver hydroxide is usually referred to as a hypothetical compound which exists only in solution. According to some qualitative tests, white silver hydroxide may be observed for an instant when the solutions of the soluble hydroxides are very dilute. It seems uncertain whether the existence of this compound has merely been inferred from the properties of the corresponding copper derivative or whether it has actually been identified.

J. D. Bruce (Chem. N. **50**, 208 (1884)), on mixing a dilute solution of silver nitrate in 90 per cent. alcohol with an equivalent amount of caustic potash in alcohol at —40° F., obtained a white precipitate, but did not succeed in separating the compound unchanged. A number of papers on the properties and solubility of "silver hydroxide" have been published, but it seems that such investigations invariably apply to "moist silver oxide" as the initial substance. See, for example, Carnelly and Walker, J. Chem. Soc. **53**, 59 (1888); Böttger, Z. phys. Chem. **46**, 521 (1903); Whitby, Z. anorg. Chem. **67**, 107; A. A. Noyes and Kohr J. Am. Chem. Soc. **24**, 1141 (1902).

The methyl alcohol was then twice redistilled from an all-glass still (used only for this purpose) and was stored in a capped flask of resistance glass. It was redistilled for each individual determination recorded in table 1. A portion of 100 c.c. when evaporated in platinum left no weighable residue.

FORMIC AND HYDROFLUORIC ACIDS. (OTHER REAGENTS.)

An excellent "C. P." grade of formic acid was diluted somewhat with water and distilled after the addition of a small quantity of barium hydroxide. The product was redistilled with silver carbonate.

Formic acid, when distilled through glass, invariably left a slight white residue upon evaporation to dryness. Even after distillation from a platinum retort, a slight brownish residue remained. The platinum condenser used for this purpose gave excellent service in the distillation of hydrofluoric acid; formic acid, however, seemed to dissolve traces of some unknown material from the condenser, even after the latter had again been cleaned in a variety of ways and after the acid had been redistilled several times. Whether this contamination originated from impurities in the platinum itself, or in the gold solder in the seams of the condenser, seemed uncertain. At any rate, as soon as the condenser in question had been replaced by a seamless one of pure platinum, the distillate of formic acid left no residue upon evaporation.

After the preliminary distillations from glass the formic acid was concentrated by fractionation and finally distilled from the platinum apparatus just mentioned. The acid was freshly distilled for each determination and was stored in a platinum vessel.

Hydrofluoric acid was purified as follows: The commercial acid was treated with potassium fluoride until the filtrate gave no further turbidity with pure potassium carbonate.[9] A considerable excess of potassium fluoride was then added, the clear liquid decanted after standing for some time, and distilled from a lead still. The product was redistilled with a little potassium permanganate and the first third of the distillate rejected. After the addition of sodium phosphate the distillate was rectified

[9] As the potassium fluoride contained some silica it could not be used in this test.

again from a lead still provided with a platinum condenser. The hydrofluoric acid thus obtained was redistilled four times from an all-platinum still, that is to say, twice with a little pure silver carbonate, and finally twice alone. The product left no residue upon evaporation and was free from perceptible traces of silica, lead, iron, chlorine, and organic matter—the chief impurities to be met with in this acid.

The purification of other reagents, besides those already described, will be given as such reagents may be called for in the prosecution of this study.

THE APPARATUS.

For reasons which will become apparent in due time, the final conversions of borax into other salts had to be carried out in a flask or long-necked bulb through which a current of air was passed. Platinum proved to be the only material suitable for this purpose. The platinum bulb applicable to all essential exigencies of the problem, without being too cumbersome or too complicated, is shown in figure 4; the sketch is largely self-explanatory.

The bulb proper was 4 cm. in diameter and had a capacity of about 30 c.c. The neck was 1.5 cm. wide and the volume of the entire flask approximately 40 c.c. The inner tube, which served to send a current of air through the bulb, was fused near its upper end into a cup-shaped stopper ground into the neck of the flask and, furthermore, was provided with two annular, perforated platinum disks (as indicated in the sketch) which were 4.5 cm. apart and all but touched the walls of the neck. These disks served a threefold purpose. In the first place they acted as guides for the inner tube and thus prevented undue strain upon the ground-in stopper and insured its proper insertion. This function of the disks must not be scorned, for a ground-in, rather shallow platinum stopper of this description—although the neck be reinforced, as in the present case—is easily rendered useless and becomes a constant source of annoyance unless the two ground surfaces be in proper alignment just before closing. With the present device the stopper easily slid into its seat when the apparatus was removed from its supports. In the second place these perforated disks acted as effective "spray-guards" in preventing

mechanical loss. It is scarcely necessary to add that evaporation of solutions was always carried out at a temperature much below the respective boiling-points. Nevertheless, traces of dissolved air, upon being expelled on warming, may cause serious loss, which will be entirely prevented by these plates. Finally these perforated disks serve to prevent a flame at the mouth of the bulb from "striking back." As will be explained later, the alcoholic vapors expelled in the volatilization of boric acid were ignited from time to time.

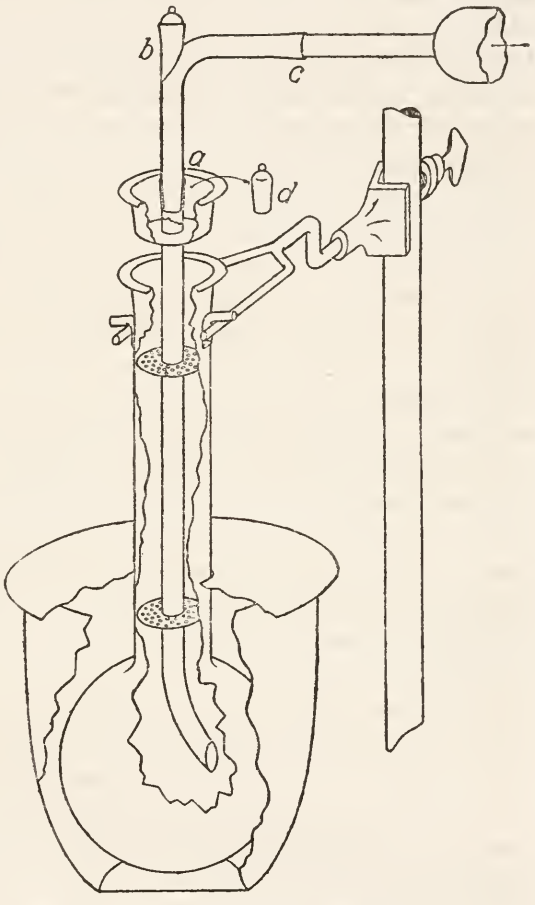

FIG. 4.

The method of supporting the bulb during the experiment is indicated in the sketch. Two stout lugs, diametrically opposite and fused to the upper part of the neck, rested on the prongs of a fork made of heavy platinum wire. The advantages of this device over any other method of support are too obvious to be detailed. The flange of the cup-shaped stopper, carrying the inner tube, rested on a similar fork. The forks were independent of each other, but they were permanently set into appropriate clamps which could be adjusted in the usual manner.

The elbow (*abc*) served to connect the inner tube to the con-

stricted end of the platinum combustion tube and gave rise to two ground joints at (*a*) and (*c*). In the final determinations this combustion tube had no particular significance. Originally it was intended to vaporize the methyl alcohol from boats placed in the combustion tube and to conduct the vapor through the bulb. However, as this method seemed to offer no particular advantages and was not easily controlled, all liquid reagents (such as water, acids, methyl alcohol) were introduced through the tubulature shown at (*b*) by means of a small platinum funnel.

In general the ground joint at (*a*) was disturbed as little as possible during a determination. When operations had to be interrupted the apparatus was disconnected at (*c*) and the bulb together with the elbow piece put on a suitable rack in a desiccator. Before each weighing, however, the elbow was removed; the bulb could then be closed completely by the hollow platinum stopper (*d*). The entire apparatus weighed about 56 grams.

It may not be amiss to add, concerning the ground platinum stoppers and connections, that manufacturers often use pumice and oil for grinding such parts, and a platinum surface so treated, of course, requires careful cleaning. In the present instance all platinum parts having ground surfaces were immersed for some time in molten sodium carbonate and then in molten potassium bisulphate; but after this treatment the joints were found to "stick" and were as useless as before. To remedy this defect the stoppers and joints were carefully reground with a mixture of pure, very finely powdered oxalic acid and glycerol. This required considerable time, as the oxalic acid acts only as a very mild abrasive. The parts thus prepared were then thoroughly cleaned and ignited and finished with a little glycerol alone. Any particles of oxalic acid which might have become embedded in the platinum were easily decomposed upon ignition. The connections obtained in this way proved very satisfactory. A proper functioning of the joint at (*a*) was imperative, because it marked the juncture between the container to be weighed and the rest of the apparatus. A number of "make-and-break" operations at this joint did not perceptibly affect the weight of the former.

The bulb was not allowed to come in contact with a direct gas flame, but was heated in an air-bath formed by a large platinum crucible. For the lower temperatures the crucible was set into a

plate of asbestos board (not shown in the sketch) covered with sheet nickel. Noxious vapors could be removed by a small hood placed over the part of the apparatus which projected above the asbestos board. This hood consisted of two well-fitting, overlapping cylindrical shells of sheet copper which, when in position, formed a complete cylinder. The latter was capped by a platinum funnel, the stem of which could be connected to an exhaust. A vertical slot, in the side of the cylinder, served for the introduction of a thermometer, or pyrometer, to roughly measure the temperature within the air-bath. In the stronger ignitions, such as were necessary in fusing the salts, the asbestos board was dispensed with; but the bulb was protected by a crucible, which in this case rested on a triangle and could be covered with a platinum lid consisting of two overlapping sections. In this manner the heat was concentrated on the bulb proper without overheating the neck.

The current of air which passed through the apparatus during an experiment was produced by a water blast. Before reaching the pump the air was drawn through a solution of caustic soda. It was then conducted through a solution of potassium permanganate containing potassium hydroxide, and next through moist soda-lime, fused caustic potash, concentrated sulphuric acid, and finally, before reaching the platinum combustion tube, through a tower filled with freshly fused caustic potash. The train was constructed entirely of glass. The plug of the combustion tube was provided with a platinum inlet tube which was joined to the glass train by means of a "glass spring," the free end of which was ground into the metal tube.

THE DEHYDRATION OF BORAX.

For obvious reasons it seemed desirable to refer the analyses of borax to the anhydrous salt. It was found, however, that the complete expulsion of water from borax is no simple matter. The observations of Dobrovolsky in 1869, concerning the dehydration of this salt, seem to have attracted no attention until they were mentioned by Brauner in 1906.[10] According to Dobrovolsky only small quantities (0.1 to 0.3 gram) of borax can be dehydrated completely, whereas larger quantities retain water.

[10] In Abegg's Handbuch d. anorg. Chem., Vol. III, part 1, p. 6.

The dehydration of this salt was studied more fully by Hoskyns Abrahall,[11] in 1889. He found that when borax was heated to between 250° and 300° for 20 hours, under reduced pressure, about 0.5 per cent. of water still remained, but that "practically the whole of the water that could be expelled at this temperature came off in the first 3 or 4 hours."[12] It is interesting to note that this chemist condensed all the water given up by a sample of crystallized borax heated to 265° in a vacuum. This water "did not act on turmeric paper and left no appreciable residue when left to evaporate in the cold over sulphuric acid." The crucible containing the borax was then heated over a direct flame, first over a Bunsen burner and finally over the blast-lamp, and in two instances in a small Fletcher furnace capable of melting cast iron. However, Abrahall's experiments show that, depending upon the mode of heating, appreciable and varying quantities of borax were volatilized; hence he concluded that the dehydration of borax was untrustworthy for the derivation of an atomic ratio. (See also quotation on p. 52).

A number of experiments relative to the volatility of borax, upon fusion, were carried out by Waldbott [13] for practical and general analytical purposes. He discovered, for example, that a portion of borax glass, weighing about a gram, lost 14 per cent. when heated over the blast-lamp for 3 hours and that a quantity of fused borax (cir. 12.0 grams), kept in a kiln at about 1400° for 60 hours, lost almost 50 per cent. of its original weight. Incidentally, it may be mentioned that, from several analyses of the residues, Waldbott drew the conclusion that no segregation takes place during fusion, but that the salt is volatilized as such, *i.e.*, as $Na_2B_4O_7$. This flatly contradicts Leonard,[14] who states that "the residue contains rather less soda than that required for the formula $Na_2B_4O_7$, and that the residue is not constant."

Waldbott's observations in this particular are probably more

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[11] J. Chem. Soc., 61, 650 (1892). The paper was edited and published by Ewan and Hartog.

[12] More recently, J. Hoffman (D. Chem. Ind. 39, 411–412 (1917), has studied the progressive dehydration of borax at various temperatures (from below 100° to 318°) and finds that the final molecule of water is exceedingly tenacious, according to an abstract published in the J. Chem. Soc. 112, II, 206.

[13] J. Am. Chem. Soc., 16, 410–418 (1894).

[14] Chem. N. 77, 104 (1898).

reliable than those of Leonard, who gives no experimental data besides stating that his conclusions were based upon the titration of borax before and after fusion in a crucible for several hours, and that the residue required less standard acid for exact neutralization than did the original borax glass. Such a titration does not necessarily prove that the portion volatilized had a composition different from that of borax, for, during a protracted ignition over a gas flame, the contents of the crucible might have absorbed appreciable quantities of sulphur dioxide and, as a result, required less acid for neutralization. Waldbott analyzed the residual borax by expelling the boron with ammonium fluoride and weighing the alkali as sodium sulphate.

Although any possible absorption of sulphur from the flame was also overlooked by Waldbott, it is easily seen that such an error would have had less effect upon his analyses than upon the titrations made by Leonard. However this may be, it is certain, and not at all surprising, that borax can not be kept fused for any considerable time without loss. Our best criterion of complete dehydration is constancy of weight after several ignitions. Obviously this criterion could not be applied to borax which was being fused in an open vessel, such as a crucible or dish—the only vessels used in this particular instance in the past. The final dehydration of borax, therefore, was carried out in the apparatus already described, (p. 12). Completely dehydrated borax could be kept fused in this vessel for hours without any loss of the salt itself. A receptacle of this description was also well adapted to the subsequent volatilization of boric acid.

The general plan pursued in the dehydration of borax may now be given. The pure decahydrate, immediately after centrifugal draining, was placed in a desiccator containing caustic potash. The latter served the double purpose of protecting the salt from the carbon dioxide of the air and of removing part of the water of crystallization. In some instances it was found that the borax, consisting of a fine crystal meal, had been converted into the pentahydrate by this treatment. The latter salt is better suited for the subsequent expulsion of water, as it does not dissolve in its water of hydration and does not intumesce to such a marked degree as the deca-salt. This salt was placed in a rather capacious (150 c.c.) platinum crucible with a perforated lid, through which

a platinum tube was inserted, thus making the device resemble a Rose crucible. It was set into a plate of asbestos board covered with sheet nickel and was heated by means of a ring-burner which supplied the heat mainly to the sides of the vessel. In this manner the crucible and contents were kept at a gentle heat for several hours, while a steady stream of dry air free from carbon dioxide was passed through the apparatus. Finally the heat was increased sufficiently to melt the porous, silky mass to a clear glass. The residue was then again fused completely over a direct flame and allowed to flow toward the edge of the crucible. The mass thus collected on the side cracked sufficiently of its own accord on cooling, and a convenient sample could easily be removed for further treatment. The exclusion of carbon dioxide in the dehydration and fusion of this salt is probably not essential, because any absorption of this gas would be counteracted by the boric acid under these conditions. Nevertheless it seemed best to exclude this gas as much as possible.

This clear, flawless mass, often called "borax glass," is generally assumed to be anhydrous sodium tetraborate. A portion of such borax glass, however, weighing 1.22243 grams, was transferred to the platinum bulb already described and was kept fused for about 15 minutes; it then weighed 1.22191 grams. This process of re-fusing and re-weighing was repeated a few times until the weight finally became constant at 1.22106 grams, showing that the borax glass had given up fully 0.1 per cent. of volatile matter. As will be seen, this loss usually amounted to about 0.2 per cent. At least an hour of actual fusion was required for a 1-gram sample to reach constant weight.

The question naturally arose whether this decrease in weight was to be attributed to the loss of water. It certainly was not due to the volatilization of borax or some other compound of sodium, for during the entire fusion a sodium flame could not be obtained at the mouth of the bulb—a most delicate test which, by actual experiment, was found to show unweighable amounts of borax, unless the lower part of the bulb was heated almost to a white heat and the air current accelerated considerably.[15]

[15] This "flame test" was applied as follows: From time to time a small, pointed Bunsen flame was played across the mouth of the platinum bulb. The gas was filtered through cotton wool before reaching the burner, which was constructed

It seemed entirely possible that this final loss was due to the volatilization of boric acid. It is true, Abrahall had shown that up to 265° no volatilization of this component took place during the expulsion of water of crystallization. This observation, however, gave no clue as to what might take place at or above the fusion temperature. As any possible trace of boric acid could not conveniently be tested for directly, under the conditions, the entire question was disposed of by the following simple experiment.

A sample of "borax glass," weighing 1 gram, was fused in the platinum flask in a stream of dry air until its weight was constant. A small quantity of pure water was then added and the contents digested at a gentle heat for many hours. The water was finally evaporated very slowly and the residue again fused to constant weight. The latter was 0.026 milligram in excess of the final weight recorded just before the evaporation with water. In other words, the two final weighings before and after the treatment with water were identical, for the apparent difference found did not exceed the experimental error in weighing. It should be added that the second dehydration of the borax required fully as much time and effort as the first. This experiment seemed to justify the conclusion that, by the method indicated, borax can be completely dehydrated without any loss of the salt itself, that no boric acid is volatilized with the water, and that *the final loss sustained by borax glass upon fusion is due entirely to the removal of the last traces of water.*

In some experiments it was found that the borax had actually begun to vaporize within the bulb, for a distinct film of fused borax was noticeable on the end of the inner platinum tube; however, as the long neck of the bulb remained comparatively cool, no weighable quantities of the salt had left the apparatus. This water, it should be added, was not hygroscopic water, which might have been taken up just before the substance was transferred to the bulb, but represented the last portion of the original water of crystallization. Pure borax glass was found to be prac-

of narrow-bore nickeled brass tubing and was kept scrupulously clean. Such a flame was also used occasionally to ignite the vapors escaping from the bulb in the final treatment of the residues with methyl alcohol. Crude as it may seem, this method of testing proved quite satisfactory and, as carried out, precluded the possibility of contaminating the contents of the bulb.

tically non-hygroscopic under ordinary conditions. Beads of this substance were exposed to the air for months without losing their luster, and a sample fused in a crucible and spread around the sides gained only 0.006 per cent. when exposed for 3 hours; even after 20 hours it had gained only 0.014 per cent.

The final dehydration of borax by fusion to constant weight is of the greatest importance in the present work. It accounts very largely, if not entirely, for the new value found for the atomic weight of boron, for it will be shown that if the analyses in the present investigation had been referred to the roughly dehydrated "borax glass," the apparent atomic weight of boron would have been practically 11.0 (see p. 43). The method of dehydration noted above was strictly adhered to in each case and constitutes one of the most important steps in the analysis. In this manner pure anhydrous sodium pyroborate was probably obtained for the first time without the loss of some of the salt itself by volatilization. It is of interest to observe that the completely dehydrated product could be kept fused in the bulb for hours without appreciable change in weight, even when a slow current of air passed through the apparatus. It would seem that anhydrous borax is one of the most stable alkali salts under these conditions.

CONCERNING THE COMPLETE DEHYDRATION OF BORAX.

That borax, even in a state of fusion, should retain appreciable quantities of water is noteworthy and suggestions as to the reason for this peculiar behavior may properly be offered at this time. Substances which part with the last portions of water only upon prolonged ignition and at elevated temperatures are, of course, well known, and the difficulties involved in the complete dehydration of certain minerals, of silica and alumina (to mention only a few), are known to every analyst. Such substances as these, however, are "infusible"; hence, the difficulty just referred to is not entirely unexpected.

Salts, on the other hand, may, as a rule, be considered completely dehydrated as soon as a state of fusion has been reached. Not so with borax. Here the analyst is confronted by the peculiar fact that about 99.8 per cent. of the water of hydration can be driven off with ease, whereas 0.2 per cent. or less is removed

only with great difficulty, although the salt is kept in a complete state of fusion and although anhydrous borax is not particularly hygroscopic. The rather artificial distinction between "water of crystallization" and "water of constitution" can be of little assistance in this case and amounts to begging the question. It would lead to the rather extravagant conclusion that only about $\frac{1}{500}$, or even less, of the water originally present was "water of constitution." The experimental fact may be explained, it is thought, in a much simpler and more reasonable manner.

Practically nothing is known concerning the state or form in which water, or the elements of water, exist in hydrated salts, and it matters little in this discussion. Certain it is that such water of crystallization escapes as vapor when the salt is heated, and that in many instances when the loss of water begins at a rather low temperature this water must pass through the liquid state before escaping as steam. At some stage, then, during the dehydration of borax there must be minute particles or globules of water momentarily in contact with sodium borate, which would mean, of course, so many droplets of dissolved borax in contact with the solid. Now these droplets, or this "mist" of borax solution, distributed through the porous mass of partly dehydrated borax, must have the properties of an ordinary borax solution; hydrolysis, for example, must take place as usual. It is well known that there are good reasons for assuming that borax in water solution is extensively hydrolyzed, that is to say, that this solution is the scene of such reactions as the following:

$$Na_2B_4O_7 + H_2O \rightleftarrows 2NaBO_2 + 2HBO_2$$
$$Na_2B_4O_7 + 3H_2O \rightleftarrows 2NaOH + 4HBO_2$$

Such or similar reactions would naturally take place in the "mist" referred to above; and it is true that hydrolysis gradually decreases and finally disappears as we evaporate the solvent; in the present case the metaborate or the hydroxide of sodium combine again with the boric acid to form the original sodium borate. Bearing in mind, however, that the complete combination of sodium hydroxide and the very weak boric acid takes place quite slowly, it is not unreasonable to suppose that in the evaporation of the droplets of borax solution the expulsion of the water may be comparatively rapid on account of the minute quantities

involved, whereas the recombination of the base and the acid is relatively slow. In other words, the re-formation of borax, under such conditions, may lag behind, as it can not keep pace with the evaporation of the solvent. Thus it would seem quite conceivable that the original globules of borax solution, upon evaporation, would leave minute residues containing some uncombined sodium metaborate (or hydroxide) and boric acid. The latter combine very slowly, on account of the weak nature of the acid, and the union is complete only after prolonged fusion.

According to this view the last traces of water expelled from fused borax are not merely the last portions of the water of crystallization proper, but are rather to be looked upon as water of neutralization, resulting from the recombination of sodium metaborate (or hydroxide) with boric acid, both of which were produced by a transient hydrolysis during the earlier stages in the dehydration; and this view explains why the last traces of water should be removed with greater difficulty than the bulk. Hence, the final loss of water in the dehydration of borax may, in all probability, be due to the completion of such reactions as the following:

$$2\,NaBO_2 + 2HBO_2 = Na_2B_4O_7 + H_2O$$
$$2\,NaOH + 4HBO_2 = Na_2B_4O_7 + 3H_2O$$

The preceding remarks seem to justify the general conclusion that many other salts which are extensively hydrolyzed in water solution should also show an anomalous behavior when deprived of the last trace of their "water of crystallization." Such, indeed, appears to be the case. Every chemist is familiar with the difficulties encountered in drying sodium carbonate without decomposing some of the carbonate itself. Undoubtedly the anhydrous substance itself begins to dissociate in this case and thereby suffers a loss of carbon dioxide; moisture, however, seems to aggravate this loss and to cause some carbon dioxide to be given off at a lower temperature. Again, in the work upon the atomic weight of columbium,[16] it was found quite difficult to dehydrate sodium metacolumbate ($Na_2Cb_2O_6.7H_2O$) completely. This salt, which is also strongly hydrolyzed by water, had to be ignited for 10 hours or more before constant weight was reached. As this salt is

[16] J. Am. Chem. Soc. 37, 1793 (1915).

infusible, any columbic acid (a very weak acid) and sodium hydroxide produced by a transient hydrolysis might find it particularly difficult to recombine and form the original columbate and water. Hence, the prolonged ignition.

In the special case of borax the last portion of water may also be assumed to be held in a somewhat different manner, which would not require the supposition of any hydrolytic action. Borax, in a state of fusion, is often said to dissociate into sodium metaborate and boric anhydride:

$$Na_2B_4O_7 \rightleftarrows 2NaBO_2 + B_2O_3$$

This dissociation may conceivably commence before the water has been driven out completely. The hygroscopic boric anhydride would naturally combine with any water still present and thus retard the final dehydration.

This question of the complete dehydration of borax has been discussed at some length here because previous investigators have made extensive use of fused borax in atomic weight work without fully realizing the difficulties presented by the dehydration of this salt. The question, therefore, is all-important. The results obtained in the present investigation, as previously indicated, hinge upon this very point.

BALANCE AND WEIGHING; CONSTANTS USED.

All weighings were made on a Troemner balance No. 10, which was kept in a double case and was easily sensitive to 0.02 mg. The weights were carefully calibrated by the substitution method.

Weighings were made by comparing the platinum bulb containing the substance, by substitution, with a counterpoise consisting of a stoppered platinum bottle which had approximately the same weight and surface as the former. Weights from a second set served as a tare on the other balance pan. The counterpoise was also ignited (protected from the free flame, of course) before each weighing; both objects, having nearly the same initial temperature, were then allowed to cool, side by side, in a large desiccator placed near the balance case for at least 4 to 5 hours. The stoppers were inserted just before weighing was begun. When the bulb had reached constant weight, which usually required about an hour, it was substituted by the counterpoise, which had

been exposed to the same conditions for the same length of time. The difference between the objects was thus determined.

The densities used in the reductions to vacuum for the various substances involved are given below. They refer to the fused salts.

	Density.		Density.
$Na_2B_4O_7$	2.357	Na_2CO_3	2.533 [19]
NaCl	2.161 [17]	NaF	2.804
Na_2SO_4	2.698 [18]	Brass	8.40
$NaNO_3$	2.255		

The density of sodium borate (which had been fused in a double platinum crucible for several hours) was determined in toluene. It was found that 3.8607 grams of the salt displaced 1.4103 grams of toluene at 25°. The density of the toluene at the same temperature was 0.8610, referred to water at 4°. From these data 2.357 [20] is deduced as the density of fused borax.

The density of fused sodium nitrate was determined in a similar way. It was found that 8.2077 grams of this salt displaced 3.1344 grams of toluene at 25°. This yields 2.255 for the density of fused sodium nitrate.

For fused sodium fluoride, 5.1199 grams displaced 1.5739 grams of toluene at 25°; 6.6544 grams displaced 2.0414 grams of toluene. Hence, the density of the salt was found to be 2.801 and 2.807, respectively. The average, 2.804, was taken as the density of fused sodium fluoride. The weights given in these determinations refer to the vacuum standard.

The antecedent atomic weights used in calculating the atomic weights of boron and fluorine are the following:

O = 16.000	S = 32.069
Na = 22.997	N = 14.010
Cl = 35.457	C = 12.005 [21]

[17] Baxter and Wallace, J. Am. Chem. Soc. **38**, 261 (1916).
[18] Richards and Hoover, Ibid. **37**, 111 (1915).
[19] Ibid., p. 105.
[20] For present purposes this agrees well with the value 2.367 found by Filhol (Ann. chim. phys. (3) **21**, 415 (1847)). Ramsay and Aston (J. Chem. Soc. **63**, 210 (1893)), found 2.29; this seems to indicate that the sodium borate was not entirely free from water.
[21] This value has been questioned by E. Moles (J. chim. phys. **15**, 51 (1917)). It is the value obtained by Richards and Hoover, J. Am. Chem. Soc. **37**, 106 (1915). As other determinations on record also point to a somewhat higher value than 12.00, it seemed safe enough to use the value given above.

The third decimals in the above values are uncertain. However, as the atomic weights of boron and fluorine were to be calculated to three decimals, and since these two values are roughly of the order of magnitude of the antecedents, it seemed reasonable to assume the latter also to the third decimals. The above fundamental values were decided upon before the final calculations were made. Whether another set of values would have led to a more concordant series of results for boron is of little consequence in the present case. If the methods applied in this investigation were to furnish a severe check upon the fundamental atomic weights used, a much larger number of individual determinations would have been necessary (see table 1, p. 42). For the determination of the atomic weights of boron and fluorine, however, the number of experiments seems adequate.

CHAPTER II.

A. THE ATOMIC WEIGHT OF BORON.

PRELIMINARY EXPERIMENTS.

In the preliminary experiments one sample of commercial, thrice recrystallized borax was converted into sodium fluoride by a method to be outlined in the following paragraphs, while another sample was changed to sodium chloride by an analogous method. These conversions were made in a platinum crucible of 35 c.c. capacity and showed that the method, carried out in this manner, will yield excellent results for ordinary analytical purposes. However, in these instances, ordinary "borax glass" was used, borax which had not been fused to constant weight. There were, of course, other quite obvious reasons why the final determinations could not be conducted in a crucible—such as the volatility of the halides of sodium (particularly that of the fluoride) and the impracticability of properly applying the "flame test" [1] for boric acid.

Three conversions of borax were then effected in the platinum bulb described in Chapter I. In these analyses a special preparation of borax was used (see p. 8); the samples thus analyzed, however, were not considered to be of the degree of purity desired, as they had been removed before the borax was fused and recrystallized for the final work. These experiments were merely intended to thoroughly test the apparatus and to give practice in the various manipulations involved. It may be added, however, that these three preliminary experiments (in which the borax was dehydrated completely) also supported the low value for boron finally derived. Nevertheless the results, for the reasons just stated, have not been included in table 1. The final experiments to be recorded in the following pages, therefore, begin with experiment IV, *i.e.*, the first experiment in which the final and best preparation of borax was used.

In the following description of the individual analyses the number of the experiment refers to the corresponding number in

[1] See note on page 18.

table 1, which gives the results in the order in which they were obtained; none have been omitted. In this account, however, the experiments, involving identical operations, have been described collectively.

In some instances the weight of the original "borax glass" was also determined and may be found in the table. Unfortunately, this preliminary weight was not taken in every case, for the exact amount of the residual water, at first, seemed of little importance, the chief object being to remove the water completely and to make truly anhydrous borax the initial substance. Later it was realized that very important conclusions were to be drawn from the quantity of such residual water; its significance is evident from table 2 and will be discussed in due time.

FINAL DETERMINATIONS.

Experiment IV: The Ratios Between Sodium Tetraborate, Sodium Chloride, and Sodium Sulphate.

The distillation of anhydrous borax with hydrochloric acid and methyl alcohol had been utilized by Ramsay and Aston in deriving the ratio of sodium borate to sodium chloride. The results obtained by them will be discussed in Chapter III. In the present case it seemed well to determine the ratio $Na_2B_4O_7$: 2NaCl by a method strictly analogous to that leading to the ratio $Na_2B_4O_7$: 2NaF, for in addition to the direct ratios the relation NaCl : NaF, by cross-reference, was to be used. As previously indicated in Chapter I, the conversion of borax into sodium fluoride was most easily effected indirectly through the formate, a method which will be described more fully in the next experiment. Hence, the conversion of borax into sodium chloride also was to include the use of formic acid.

As the general procedure in the final dehydration of borax was the same in all determinations, it will be outlined before the experiment proper is described.

The empty bulb (protected from the direct flame) was strongly ignited for at least 30 minutes while a current of dry air passed through the apparatus. It was weighed and ignited again until two consecutive weighings did not differ more than 0.02 milligram, approximately. With the empty bulb such an agreement could usually be obtained after two ignitions. The jacketing of the

bulb during such an ignition is, of course, highly important. The term "constant" weight, as used in the sequel, should be taken to imply a variation of not more than 0.03 milligram, unless otherwise stated. A much closer agreement was often observed, but in view of the experimental error in weighing such instances must have been largely accidental.

A sample of "borax glass"[2] was now transferred to the bulb and kept fused in a current of dry air, free from carbon dioxide, until its weight was constant. Needless to say, the inner platinum tube, after the introduction of borax, was not again removed until the entire experiment had been completed. It was found that one gram of vitreous borax must be kept fused in this manner for about an hour before it is worth while to take its weight. It was then re-fused for a period of from 20 to 40 minutes, depending on the size of the sample. In experiment XI, for instance, the vitreous borax (after the preliminary weighing) was kept fused for fully 90 minutes before reweighing. It still contained 0.1 milligram of water; for, after another fusion lasting 40 minutes, the weight decreased by this amount. Another fusion, again of 40 minutes' duration, produced no further change in weight. The flame of a large grid-burner served as a source of heat; the time given refers to actual fusion. It should be added that the final weight of the fused borax could in every case be fixed with great precision. Numerous weighings and refusions showed that the weight remained quite constant after the water had once been expelled.

The anhydrous borax thus obtained was digested, at a gentle heat and for many hours, with a few cubic centimeters of purest water. The quantity of water, as a rule, was sufficient to completely dissolve the borax at 70°. Solution could be facilitated by gentle agitation, as the bulb at this stage of the analysis was not connected with the combustion tube. A slight excess of formic acid (see p. 11) was then added and the mixture very slowly evaporated to dryness in a current of air. As the contents of the bulb were concealed from view and the progress of the reaction could not be directly observed, ample time had to be allowed. The dry residue was next digested with a few cubic

[2] The preliminary dehydration of borax has been described in Chapter I.

centimeters of methyl alcohol (see p. 9) and the methyl borate gradually expelled in a current of air. Air proved entirely satisfactory for this purpose and showed no tendency to form explosive mixtures. At first the air-bath (*i.e.*, the outer platinum crucible) was kept at a temperature of about 50°, which was raised very slowly. Finally, when no more alcoholic vapors were given off, the temperature was gradually increased to about 110°, or even a little higher.

After cooling, the evaporation was repeated several times with fresh portions of methyl alcohol. In each evaporation 5 to 8 c.c. of the alcohol were used and a drop of formic acid was added to the last portions. The best indication as to the progress of this volatilization of the boric acid could be obtained by igniting the vapors, from time to time, at the mouth of the bulb (see note on p. 18). The flame was easily extinguished again by interrupting the air current for a moment. As long as any considerable amount of methyl borate was present in the vapors, the flame showed the familiar green coloration. It is evident that the delicacy of this color reaction depends not only on the amount of boric acid present, but also on the relative amount of alcohol used. However, it was found that the presence of about 0.1 per cent. of boric acid could be detected in sodium formate by this flame test when only small quantities (2 to 3 c.c.) of methyl alcohol were used.

When the flame test no longer indicated the presence of boric acid, the contents of the bulb were digested with a few cubic centimeters of water and again evaporated to dryness. The treatment with alcohol was then repeated. The vapors, when ignited, again showed a very faint green at first. Two more evaporations with 2 c.c. of water, followed by treatment with several portions of about 3 c.c. of methyl alcohol, were carried out. Five small portions of alcohol were used in the final evaporations. The total quantity of methyl alcohol used in this determination was not noted; however, it did not exceed 40 grams. In some of the later experiments the exact total was recorded.

That the residue (sodium formate) after such treatment contained no perceptible traces of boric acid was proved as follows (see also p. 3): Another sample of borax had been converted into sodium formate by the method just outlined. The residue

gave no test for boric acid with turmeric paper. A second portion of sodium formate (containing approximately 0.02 per cent. of boric acid) did respond to this test. After two evaporations with methyl alcohol, however, the turmeric test gave a negative result. As formic acid seemed to interfere with the turmeric reaction, the residues were changed to sodium chloride by evaporation with hydrochloric acid before testing for boric acid. Slight traces of the latter were probably lost in this way; if so, the value of the test was not greatly affected thereby.

To return to the description of the main experiment. Before the final evaporation with the alcohol the outside of the bulb was rinsed with a little methyl alcohol and water to remove possible traces of boric acid resulting from a slight decomposition of the methyl ester. The residual sodium formate, which undoubtedly was free from boric acid, was dissolved in a small quantity of water mixed with an excess of pure hydrochloric acid and evaporated to dryness. The formate was thus completely transposed to the chloride. In order to make doubly sure, however, the sodium chloride obtained was gradually heated to about 200° and, when cool, again moistened with a few drops of hydrochloric acid and evaporated. It was then dried very slowly in a current of air and finally fused. During the actual fusion the air current was all but stopped and gradually increased again during the slow cooling. The salt was then weighed. A second fusion, conducted as the first, produced no appreciable change in weight.

The hydrochloric acid used in this transposition was obtained by allowing pure concentrated sulphuric acid to drop into strong hydrochloric acid (method of Hare) free from arsenic and other appreciable impurities. The hydrogen chloride gas thus released was washed with concentrated hydrochloric acid and allowed to fill a closed vessel containing a quartz dish with pure water. A solution of hydrogen chloride was thus obtained by direct contact of its components, without the use of a delivery tube. The apparatus was constructed entirely of glass and the quartz dish had previously been subjected to a prolonged action of hydrochloric acid.

After the sodium chloride had come to constant weight it was evaporated with a moderate excess of pure sulphuric acid.

In order to insure a complete interaction the residue, after the expulsion of the hydrogen chloride, was dissolved in a little water and concentrated by evaporation. Finally the temperature was gradually raised to expel the excess of the acid. The last traces of sulphuric acid were removed by keeping the sodium sulphate in a state of fusion for some time. The evaporations were accelerated by a current of air. When the sodium sulphate had been kept fused for about 30 minutes the bulb was lowered so as to bring the lower (curved) end of the inner tube within the neck of the bulb. This part of the inner tube could thus be raised to a much higher temperature and the complete removal of the acid and decomposition of possible traces of bisulphate be made certain. These operations were then repeated. It was found that after the free sulphuric acid had once been expelled in this manner, the weight of the normal salt remained remarkably constant, even after prolonged fusion in the jacketed bulb, with a current of air passing through the latter.

After the completion of the experiment the sodium sulphate was dissolved in a little water. The solution was neutral to methyl orange; the addition of a trace of dilute hydrochloric acid produced a pink tint. In converting the sodium chloride into the sulphate an excess of sulphuric acid was not to be avoided and the complete removal of this excess proved rather laborious. Nevertheless the results and the test show that the method was entirely reliable.

The sulphuric acid used in this experiment, and in those to follow, was prepared by distilling an excellent "C. P." grade from a long-necked Jena retort. Only the middle portion of the distillate was collected and redistilled as before. The acid was diluted and used as indicated.

Experiments V, IX, X, XI: The Ratios Between Sodium Tetraborate, Sodium Fluoride, and Sodium Sulphate.

The method finally adopted to convert borax into sodium fluoride has been indicated in Chapter I. That the direct conversion of the borate into the corresponding fluoride by means of hydrofluoric acid and methyl alcohol was most unpromising has also been emphasized. There was still another method which seemed to be entitled to a fair trial. This consisted in igniting a mixture of powdered borax and ammonium fluoride, whereby

volatile ammonium borofluoride (NH_4BF_4) and sodium fluoride are produced. Reischle[3] recommended this procedure for the indirect determination of boric acid in borax, the only difference being that he prefers to finish with sulphuric acid and to weigh the resulting sodium sulphate.

The determination, according to Reischle, is carried out as follows: Powdered borax (the decahydrate) is mixed with six times its weight of resublimed ammonium fluoride and gently heated. The major portion of the boron is thus expelled as ammonium borofluoride. After cooling, the residue is evaporated with sulphuric acid, which, as the author states, removes the last traces of boron fluoride and ammonium borofluoride. According to Reischle this method is superior to all others, including Gooch's distillation method. By the latter method Reischle found from 90.8 to 101.0 per cent. of the boric acid present. Without discussing the pros and cons, it seems entirely proper to say that these poor results are not entirely chargeable to the Gooch method.

The ammonium fluoride method has also been adopted, and found satisfactory, by Waldbott[4] in the analysis of borax. The method may be of great value for ordinary analytical purposes; for the derivation of a ratio it was soon discovered to be of little promise.

In the present instance the initial substance, the substance which had to be weighed, was fused borax. In order to produce a thorough mixture with the reagent the anhydrous borax was dissolved in water and evaporated with an excess of ammonium fluoride, which was added either in solid form to the concentrated borax solution or in the form of a solution obtained by combining pure hydrofluoric acid with redistilled ammonia. It was found that the resulting mixture is evaporated to dryness with great difficulty, for even when the apparatus was heated in an oven the formation of crusts retarded the evaporation to an annoying degree. Several such treatments would have been required to make sure of the complete removal of the boron with the production of pure sodium fluoride, the weight of which was to be determined before it was converted into the sulphate. In the final ignition, furthermore, appreciable quantities of sodium fluoride were volatilized, a loss which is probably aggravated by the repeated sublimation

[3] Z. anorg. Chem. 4, 111–116 (1893). [4] J. Am. Chem. Soc., 16, 410–418 (1894).

of rather large quantities of ammonium salts. The method therefore was not suited to an atomic weight determination.

The principle of the method finally adopted for the conversion of sodium borate into sodium fluoride has been used in experiment IV, where it was applied in the corresponding conversion, involving sodium chloride as an end-product. The method depends on the facts (1) that formic acid reacts "normally" with a solution of borax, that is to say, it liberates boric acid with the production of sodium formate without any disturbing secondary reactions; (2) that sodium formate is easily transposed to a halide by evaporation with a haloid acid.

It may not be amiss to add a few more words as to the applicability of formic acid in this reaction. In the mere expulsion of boric acid by the volatilization method, irrespective of the composition of the residual sodium salt, acids other than formic may, of course, be used to advantage. In the present case, however, the remaining sodium salt was to be the fluoride, and here formic acid served admirably, if only as a "go-between." In view of the fact that the direct use of hydrofluoric acid presented many difficulties (see p. 2) it would perhaps be difficult to find another acid more suitable than formic as an auxiliary reagent in the conversion of borax into sodium fluoride.

The chief advantages of formic acid for this purpose seem to be the following: The sodium salt of this acid is most easily dehydrated, and therefore, in the present instance, the only water present in the dry residue (consisting of sodium formate and boric acid) is in combination with the latter, probably forming metaboric acid. A minimum of free or loosely combined water, of course, is favorable to the formation of the boric ester when the mass is treated with methyl alcohol. It has already been mentioned that acetic acid, for example, would not answer as well because its sodium salt is dehydrated with difficulty and at a much higher temperature. In the second place, sodium formate is exceedingly soluble in water and also soluble in methyl alcohol. Consequently, only small quantities of water need be used when the residue is dissolved and evaporated in order to expose fresh surfaces before another treatment with the alcohol. The solubility of the formate in the alcohol also facilitates the interaction of the substances in question.

Possibly the only drawback involved in the use of formic acid, at this stage of the reaction, is its volatility—a property, however, which it shares with a number of other available acids and which is of the greatest importance in the final transposition of the formate to the fluoride. The volatility of formic acid, it is true, favors a slight reversion of the original reaction between this acid and borax; that is to say, sodium formate and boric acid, in very concentrated solution or in the dry state, tend to react again (when heated) with the re-formation of some sodium borate. The extent of this reversion, however, is not alarming under the conditions and is easily counteracted by the addition of a drop or two of strong formic acid to the alcohol in the subsequent evaporations, particularly to the last portions of alcohol used. This mode of procedure insures the complete decomposition of the last traces of borax and was adhered to throughout the work.

The complete removal of the boric acid was carried out exactly as indicated in the description of experiment IV and need not be repeated. It may be of interest to indicate the quantities of methyl alcohol used in some of these experiments. In experiment IX 82 grams of methyl alcohol were used. This represents the total and includes the final portions which were practically superfluous. The total quantities of methyl alcohol used in experiments X and XI were 61 and 85 grams, respectively. Considering the quantities of boric acid that had to be expelled these amounts of methyl alcohol actually used seem rather moderate.

The sodium formate was now ready to be converted into the fluoride. It was therefore dissolved in a small quantity of water, an excess of pure hydrofluoric acid (see p. 11) added, and the mixture slowly evaporated to dryness in a current of air. The residue thus obtained was finally heated to about 200°, allowed to cool, and again moistened with a little strong hydrofluoric acid. After the expulsion of the latter it was quite safe to assume that the residue consisted of pure sodium fluoride. In the preliminary experiments it was found that, for most purposes, a single evaporation of the dry, porous formate with an excess of strong hydrofluoric acid is quite sufficient, for subsequent treatments with the haloid acid produced no appreciable change in weight.

To be doubly sure of the complete conversion of the formate,

proceed as follows: After the first evaporation with hydrofluoric acid ignite the residue gently; any possible residual particles of sodium formate are hereby decomposed and changed to the carbonate, which is then easily decomposed by a second evaporation with hydrofluoric acid. A decided excess of hydrofluoric acid is desirable in this transposition in order to produce the acid sodium salt, which is much more soluble than the normal salt. The acid salt crystallizes without water and is easily dried. Upon further ignition hydrogen fluoride is expelled, which, on account of its eagerness to combine with water, carries with it the last traces of the latter. The drying of sodium fluoride presents no particular difficulties, although it became necessary to fuse the salt before the final weighing, for the normal salt produced by the decomposition of the acid salt is a very porous mass which was found to take up traces of moisture.

In the fusion of sodium fluoride several precautions had to be observed because this salt, in spite of its high melting-point (cir. 980°), is rather volatile and its fusion in a crucible, even for ordinary quantitative purposes, must be carried out with care.[5] Even in the present case, where the salt was contained in a long-necked bulb, an appreciable loss of sodium was observed when the salt was fused in a current of air. During the fusion, therefore, the air current was interrupted. When the mass had cooled somewhat, dry air was again allowed to pass through the bulb while the upper part of the apparatus was ignited. The entire process was then repeated. In this manner it was possible to dry and fuse the salt without loss and to re-fuse it without appreciable change in weight. The rather close concordance in the values obtained for the atomic weight of fluorine (table 3) is probably due, in no small measure, to the precautions observed in the fusion of the sodium fluoride.

The fused sodium fluoride was changed to the sulphate in a manner quite similar to the corresponding treatment of sodium chloride in experiment IV, the only difference being that in the present case the reaction proceeded more slowly. Owing to the fused condition of the sodium fluoride, traces of the latter may escape transposition even if the sulphuric acid be in excess and

[5] Some quantitative experiments on the volatility of sodium fluoride, when heated in a crucible, are due to Waldbott, J. Am. Chem. Soc., 16, 418 (1894).

even after the expulsion of this excess. It was imperative, therefore, to allow ample time for this interaction; after the first expulsion of the bulk of the hydrogen fluoride it was best to digest the residue with dilute sulphuric acid for some time before the final evaporation. This mode of procedure is particularly advisable when larger quantities of fused sodium fluoride are to be transposed. Finally the sodium sulphate was fused and weighed as described before. In the evaporation of sodium fluoride with sulphuric acid in experiment IX an accident occurred and the weight of the sodium sulphate, therefore, could not be recorded.

The solution of the residual sodium sulphate in water was neutral in reaction. In two experiments the solution was acidified with hydrochloric acid and tested with hydrogen sulphide; no precipitation of platinum sulphide was observed.

Experiment VI: The Ratio of Sodium Tetraborate to Sodium Sulphate.

In this experiment anhydrous borax was changed directly to the sulphate without the intervention of either formic or a haloid acid. The general procedure calls for little additional description. The "borax glass" was fused to constant weight. After solution in water a moderate excess of pure dilute sulphuric acid was added, the mixture digested for some time, and gradually concentrated at a gentle heat in a current of air until, finally, a temperature of about 140° had been reached; this temperature was maintained for 2 hours. The expulsion of boric acid proceeds quite readily in the presence of sulphuric acid. Even after the first evaporation with water following the first distillations with methyl alcohol, the green flame of the boric ester could no longer be obtained, which indicates that the residual quantity of any boric acid must have been quite small. Nevertheless, two more treatments with water, alternating with repeated evaporations with alcohol, were resorted to. The reasons for the ease with which boric acid is thus expelled in the presence of sulphuric acid is to be sought, no doubt, in the peculiar properties of the latter acid; its dehydrating action is favorable to the formation of the boric ester and its "strength" and high boiling-point prevent even the slightest reversion of the reaction under the conditions.

The result obtained from this experiment is of interest. In the first place, the presence of silica in the borax would have made itself felt in this analysis. It is a common impurity in

commercial borax, in which it probably exists as a boro-silicate. If an appreciable quantity of it had been present in the borax used [6] the analyses involving the use of hydrofluoric acid would have yielded a low weight for the end-product and, hence, a high atomic weight for boron; whereas the analyses not involving the use of hydrofluoric acid would have led to an end-product too high in weight and, hence, to a low atomic weight for boron. A glance at table 1 (p. 42) will show that both categories of analysis gave fairly concordant values. The difference between the results obtained in the present experiment (VI) and experiment XI, for example, is practically negligible, although it is only the latter determination which involves the use of hydrofluoric acid.

Furthermore, it may be gathered from this experiment (VI) that no appreciable quantities of sodium fluoride were lost in the other experiments, when this salt was fused, for the sulphate obtained directly leads to a result in fair agreement with those in which the sulphate had been obtained by the transposition of the fused fluoride. In general, therefore, the result of experiment VI seems to form a rather severe check upon the analyses which included the formate and fluoride of sodium as intermediate products.

EXPERIMENT VII: THE RATIO OF SODIUM TETRABORATE TO SODIUM NITRATE.

The procedure followed in this experiment was analogous to the scheme outlined in the other determinations. The borax, fused to constant weight, was dissolved in a little water and the boric acid set free by the addition of an excess of pure nitric acid. The mixture was evaporated to dryness and subjected to a number of distillations with methyl alcohol until free from boric acid. The residue was redissolved in water, evaporated to dryness, and again treated with several portions of methyl alcohol. This series of operations was repeated once more; occasionally a drop of nitric acid was added to the alcohol. A grand total of 56 grams of methyl alcohol was used in this experiment.

After the evaporation of the last portion of alcohol the residue,

[6] In the present instance it is only from the sodium carbonate used that any silica might have been introduced into the borax. However, the method used for the purification of the sodium carbonate has been found to remove silica quite effectively.

consisting of sodium nitrate, was dried in a current of air (the temperature finally reached was about 200°) and weighed. This gave the weight of the unfused salt, after which the sodium nitrate was dissolved in a little water containing a few drops of nitric acid, again evaporated and dried, and finally fused for a moment at a temperature only slightly above the fusion point of this salt (cir. 315°). The weight of the product (the fused salt) was determined again and found to be 0.1 mg. lower than the first weight, that of the unfused salt. The mean of these two weighings was assumed to be the true weight and was used in the computation. The difference (0.1 mg.) between these weighings is considerably greater than permissible in the range of "constant" weight for the other salts. However, the difference did not seem excessive in the case of sodium nitrate, which can not be kept fused for any length of time without decomposition. The weight of the unfused salt, resulting after the evaporation of the alcohol, was probably somewhat too high on account of a trace of moisture; the weight of the salt fused after evaporation with dilute nitric acid was a trifle too low, presumably, as a result of a slight decomposition. Hence, "splitting the difference" seemed permissible in this case. It may be added that the water solution of the final product was neutral in reaction.

The nitric acid used in this experiment was prepared as follows: A good grade of sodium nitrate was recrystallized a few times until it was free from chlorides. This salt was then distilled with pure, concentrated sulphuric acid from a long-necked retort; the first third of the distillate being rejected. The middle fraction was redistilled with pure barium nitrate and again rectified. Finally the acid was redistilled, just before use, from a quartz distilling bulb.

Experiment VIII: The Ratio of Sodium Tetraborate to Sodium Carbonate.

This interesting ratio may be arrived at in various ways. Before giving the method finally adopted we may indicate at least two other attempts which seemed to bid fair to lead to the ratio desired.

First it would have been possible to expel the boric acid in the presence of formic acid and to change the resulting formate, by strong ignition, to the carbonate, which is the final product

of this decomposition by heat. Of course there were some misgivings as to the propriety (in atomic weight work) of the last step in this method; nevertheless it was given a trial. It was possible to prevent the ignition of the hydrogen and carbon monoxide produced in this decomposition and to obtain colorless sodium carbonate as an end-product. However, at the same time it was noticed that this decomposition was accompanied invariably by a slight mechanical loss, even when the reaction was conducted very slowly and with the greatest care, in the long-necked platinum bulb and in an atmosphere of carbon dioxide. At certain stages in this decomposition, evidently a very fine dust or "mist" of the sodium salt itself was formed, traces of which escaped from the bulb and thus caused the loss referred to. Such phenomena are not particularly surprising in reactions of this sort—that is to say, in decompositions by heat which involve a rather violent rearrangement within the molecule. Similar difficulties have been met with in the ignition of other substances, such as the chlorates. It is therefore evident that the quantitative conversion of sodium formate into the carbonate by ignition was practically out of the question, unless perhaps the entire apparatus had been subjected to a radical modification.

Another possibility which suggested itself was the following: The saponification of a suitable ester of carbonic acid, say methyl carbonate, by borax, with the simultaneous production of sodium carbonate and the methyl ester of boric acid. Methyl carbonate was prepared by allowing an ethereal solution of methyl iodide to react, at a gentle heat, with dry silver carbonate in a flask provided with a reflux condenser. The first distillate was fractioned a few times, and the fraction finally collected boiled at 90.5°. The yield was poor, but the quantity obtained (about 5 grams) was sufficient for a trial. A sample of fused borax was then dissolved in water, evaporated to dryness, and evaporated a number of times with a solution of methyl carbonate in methyl alcohol, while a current of air, free from carbon dioxide, was passed through the apparatus. The residue was finally tested for combined carbonic acid, but only a bare trace could be detected. The original borax was entirely free from carbonates; the trace just mentioned had probably been introduced by a little carbon dioxide in the water used in the first evaporation. The methyl

carbonate distilled off unchanged and it was quite evident that no reaction had taken place between this ester and the borax.

The method finally adopted is based on the following reaction:

$$Na_2B_4O_7+CO_2+6H_2O \rightleftarrows Na_2CO_3+4H_3BO_3$$

If a water solution of borax be treated with carbon dioxide an equilibrium will be reached corresponding to the above relation. It should be possible, therefore, to so influence this reaction as to lead to a complete conversion of borax into carbonate by a continued removal of the boric acid; which, of course, may be done by means of methyl alcohol if the amount of water present be relatively small. In fact, according to L. C. Jones,[7] the reaction can easily be influenced in this sense. This investigator did not contemplate its application for quantitative purposes and no quantitative data based thereon have been discovered. However, the reaction proceeded more readily than anticipated and its pronounced reversibility caused no particular difficulties.

The mode of conducting the experiment was as follows: After the complete dehydration and weighing of the borax it was dissolved in a little water and evaporated to dryness in a stream of carbon dioxide. The residue, which probably contained a considerable portion of the sodium as carbonate, was evaporated many times with small portions of methyl alcohol, exactly as indicated in the other experiments, the only difference being that a steady stream of carbon dioxide, instead of air, was allowed to pass through the apparatus. When the green flame of the boric ester could no longer be detected at the mouth of the bulb the residue was dissolved in water and the distillations with small portions of the alcohol were resumed. The entire cycle of operations was then repeated twice. A grand total of 84 grams of methyl alcohol was used in the determination. Finally, after long-continued drying at a moderate heat, the sodium carbonate was heated to fusion in the atmosphere of carbon dioxide which was gradually replaced by dry air as the substance cooled. This method of fusing sodium carbonate in carbon dioxide had been successfully applied by others [8] and was also found satisfactory in

[7] Am. Jour. Sci., V, 442.

[8] Sackur, Ber. 43, 449 (1910); and T. W. Richards and C. R. Hoover, J. Am. Chem. Soc., 37, 95 (1915).

the present case. A second fusion, under similar conditions, produced practically no change in weight.

The carbon dioxide used in this experiment, generated from pure dilute hydrochloric acid and white marble, was passed through a large tower containing beads, coated with moist sodium bicarbonate; through a second tower charged with moist silver carbonate; through a wash-bottle containing a solution of sodium bicarbonate and four similar bottles charged with glass beads and concentrated sulphuric acid, after which, before reaching the platinum combustion tube, it passed through a column of freshly fused granulated potassium carbonate.

TABULATION.

The results obtained in the experiments outlined in the preceding pages may now be presented in table 1. The constants used in the calculations have been given (p. 24). If it is remembered that the results are based on a variety of methods and are referred to five different antecedent atomic weights (of Na, Cl, S, C, N) the agreement between the individual determinations is satisfactory.

The objection may be raised, not entirely without justification, that each type of analysis should be represented by a larger number of individual determinations. That this would have been highly desirable is not to be denied. While it is true that any single determination in table 1 leading to B = 10.900 might be of small value, it will be admitted that, in the aggregate, these eight results, by virtue of their agreement, can not be without significance. Furthermore, it may not be irrelevant to add that each analysis, although the solitary representative of its type, was carried out with considerable care and involved no small expenditure of time and labor. These eight results, therefore, obtained by a number of different methods involving a great variety of conditions are of greater value than an equal number of determinations based on a single reaction and involving only one set of conditions. The latter plan is less likely to lay bare any constant error in the method than is the former.

In brief, the borax (there is reason to believe) was of the utmost purity and the general plan of analysis reduced the probability of introducing constant errors to a minimum; hence the final value derived for boron is probably quite near the truth.

That this new value (10.900) really does not seriously conflict with most previous determinations of this constant and in fact is actually supported by a number of them will be shown in Chapter III.

TABLE 1.

Experiment.	Weight of "borax glass" (grams in vacuo).	Weight of anhydrous $Na_2B_4O_7$ (grams in vacuo).	Acid used to liberate boric acid.	Boric acid expelled by repeated evaporation with methyl alcohol.	After removal of boric acid residues evaporated with:	Weight of salt obtained (grams in vacuo).	Salt in preceding column evaporated with:	Weight of Na_2SO_4 (grams in vacuo).	Ratio used: $Na_2B_4O_7$:	Atomic weight of boron.
IV	[0.90027]	0.89853	HCOOH		HCl	NaCl 0.52112	H_2SO_4	0.63313	(1)2NaCl	10.896
									(2)Na_2SO_4	10.905
V	↑	0.69695	HCOOH		HF	NaF 0.29042	H_2SO_4	0.49113	Na_2SO_4	10.901
VI	not determined	1.59374	H_2SO_4		H_2SO_4	Na_2SO_4 1.12315	—	—	Na_2SO_4	10.898
VII		1.86458	HNO_3		HNO_3	$NaNO_3$ 1.57250	—	—	$2NaNO_3$	10.900
VIII	↓	1.97702	CO_2		CO_2	Na_2CO_3 1.03946	—	—	Na_2CO_3	10.903
IX	[1.99615]	1.99197	HCOOH		HF	NaF 0.83003	—	—	—	—
X	[1.60535]	1.60201	HCOOH		HF	NaF 0.66757	H_2SO_4	1.12889	Na_2SO_4	10.902
XI	[2.65241]	2.64768	HCOOH		HF	NaF 1.10329	H_2SO_4	1.86597	Na_2SO_4	10.896
									Average	10.900

NOTE: The braces are to indicate that the four samples of "borax glass," although taken from the same original preparation of borax, represent three different lots that had been dehydrated independently.

THE ATOMIC WEIGHT OF BORON REFERRED TO "BORAX GLASS."

Table 2 has been compiled from data recorded in table 1. It shows how, and to what extent, an incomplete dehydration of borax (yielding "borax glass") would have affected the atomic weight of boron. It also shows that a tolerably concordant series of results would have been reached if ordinary "borax glass" had been used as the initial substance, as the average indicates that

the final value (though obviously incorrect) would have been in excellent agreement with the present value (11.0).

It should be borne in mind that the samples of "borax glass" represented in this table had not been dehydrated in one lot; they were taken from three different lots which had been dehydrated separately. Unfortunately the weight of the "borax glass" was not determined in experiments V, VI, VII, and VIII, as the true significance of the residual water was not fully realized at first. However, we have little reason to doubt that these samples of borax glass would have shown approximately the same

TABLE 2.[1]

Experiment.	Weight of "borax glass" (grams in vacuo).	Residual water, per cent.	Weight of salt obtained (grams in vacuo).		Ratio used, borax glass:	Apparent atomic weight of boron.	
						(*a*) From borax containing percentage of water observed.	(*b*) If "borax glass" had contained 0.3 per cent. of water.
IV	0.90027	0.193	NaCl: 0.52112	Na_2SO_4: 0.63313	2NaCl : Na_2SO_4	10.993 11.003	11.047 11.057
IX	1.99615	0.209	NaF: 0.83003		2NaF (F=19.005)	11.007	11.053
X	1.60535	0.208		Na_2SO_4: 1.12889	Na_2SO_4	11.007	11.054
XI	2.65241	0.178		Na_2SO_4: 1.86597	Na_2SO_4	10.986	11.048
					Average	10.999	11.052

[1] Experimental data taken from table 1.

percentage of moisture (cir. 0.2 per cent.) as the other portions. As the braces in table 1 indicate, it was (strictly speaking) only in experiments VI and VII that the residual water was not determined at all. The percentage of water in the borax of experiment XI is somewhat lower than that in the preceding sample, probably because (before it was transferred to the bulb) it had been re-fused in the crucible in which the preliminary dehydration of the crystals had been carried out.

The full significance of table 2, particularly of the last column, may be gathered from the discussion of Ramsay and Aston's determinations in Chapter III (p. 57).

B. THE ATOMIC WEIGHT OF FLUORINE.

The various salts derived from borax in the determinations recorded in table 1 may be grouped around the central substance, *borax*, in such a manner as to bring out their relation, not only to borax itself, but also to one another. This arrangement is shown in the following diagram (figure 5):

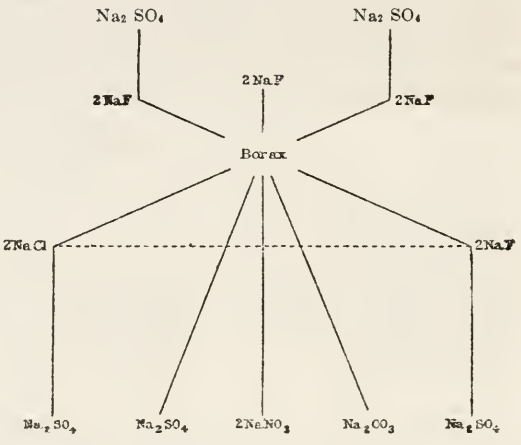

FIG. 5.

This diagram shows at a glance that the results might be correlated in a great variety of ways. It is easily seen that any two salts on different lines, radiating from borax and representing independent determinations, might be compared, indirectly, if their quantities were computed with reference to a fixed quantity, say 100 grams, of borax; the "cross-ratios" thus obtained might serve for checking purposes or for the calculation of the atomic weights of other elements besides boron. However, the experimental data did not seem to warrant the calculation of more than one additional atomic weight, namely that of fluorine. Of the possible cross-ratios only one, NaCl : NaF (indicated by a dotted line in the diagram), has been used. Eight values for fluorine have been calculated from the data recorded in table 1 and are given in table 3, together with the ratios used. In four of these the new value for boron (10.900) has been included for reference. Three values are based on the atomic weights of sodium and sulphur; one value, as already mentioned, has been computed from a cross-ratio. The agreement between the individual values is excellent and is largely due to the following factors: complete dehydration of the borax, complete elimination of boric acid, and avoidance of loss in the ignition of sodium fluoride.

In this connection it may not be amiss to add a few words concerning the value of cross-ratios in atomic weight determina-

tions. Comparisons by cross-reference have been advocated and frequently been utilized by F. W. Clarke [9] and have often furnished valuable data and checks upon experimental work. As a rule, however, the original experimenter scarcely ever determines a cross-ratio for its own sake. In most cases two compounds may be brought into direct relation without the intervention of a third. In some instances, however, such direct comparisons are most unpromising, if not impossible, for practical reasons. For such reasons, an indirect ratio, or cross-ratio, may be preferable to a direct ratio.

TABLE 3.[1]

From Exp. No.	Ratio used.	Atomic weight of fluorine.
IV and V	NaCl : NaF (cross-ratio)	19.002
V	2NaF : $Na_2B_4O_7$	19.005
V	2NaF : Na_2SO_4	19.006
IX	2NaF : $Na_2B_4O_7$	19.004
X	2NaF : $Na_2B_4O_7$	19.006
X	2NaF : Na_2SO_4	19.008
XI	2NaF : $Na_2B_4O_7$	19.005
XI	2NaF : Na_2SO_4	19.002
	Average.....	19.005

[1] Experimental data recorded in table 1 (p. 42.)

In the determination of the atomic weight of fluorine, for example, it would seem very desirable to establish its ratio to another halogen. However, since the chemistry of the halides holds forth no very promising means of comparing the fluoride of a given element directly with another halide of the same element, practically no efforts have been made in this direction. True enough, the analyses of silver fluoride by Berzelius [10] and possibly those by Fremy [11] would fall within the category; the properties of silver fluoride, however, are such as to deprive these analyses of any practical value in the fixing of the atomic weight

[9] A Recalculation of the Atomic Weights, 3d ed. (1910).

[10] Afhandlingar i Fys. Kemi Miner. **4**, 243, 455 (1815). The original paper we have not seen. The reference is that given by Brauner (in Abegg's "Handbuch"). The data are also given in Christensen's paper on the atomic weight of fluorine (Jour. prak. Chem. (2) **35**, 541–559 (1887).

[11] Ann. chim. phys. (3) **47**, 1 (1856).

of fluorine. The work of McAdam and Smith,[12] who converted sodium fluoride into sodium chloride, is the only modern determination on record which seeks to establish such a direct ratio between these two halides by chemical means. Unfortunately, their work was interrupted prematurely and the experience of those authors shows that the reaction in question did not proceed smoothly.

It would seem that the ratio of fluorine to another halogen, say chlorine, may be established much more readily by an indirect comparison—that is to say, by converting a sample of a suitable compound to the chloride, and another sample of the same preparation to the fluoride by an independent analysis. The ratio between the two halides could then be easily calculated. In the present work borax has been used as such an intermediate substance for the indirect comparison of sodium chloride and sodium fluoride. Originally it was intended to repeat the conversion of borax into sodium chloride with larger quantities of material, for in experiment IV the quantities involved are rather small, but this plan was abandoned in favor of the conversion of borax into the other salts. At any rate, even the single conversion to the chloride aids in exhibiting the applicability of the indirect method in this particular case.

Such a comparison, by cross-reference, has certain general advantages over a direct comparison. In the determination of an atomic weight, from a direct ratio, the initial substance must not only be pure in the ordinary sense, but its composition must exactly correspond to the formula assumed. In an indirect comparison, the initial substance must also be free from impurities, it is true, but the exact proportion of the elements within the compound is immaterial. In the present case the borax should consist of a union of pure Na_2O and pure B_2O_3; the exact ratio in which these two oxides are combined is of no consequence so long as we draw upon the same homogeneous preparation for analysis. Obviously the atomic weight of boron need not be known in this case.

The new value for fluorine (19.005) is considerably lower than that calculated by Clarke (19.041)[13] and also lower than that

[12] J. Am. Chem. Soc. 34, 592 (1912).
[13] Op cit., p. 408 (1910).

preferred by Brauner (19.02).[14] Jacquerod and Tourpaian [15] derived the atomic weight of fluorine from the weight of a normal liter of silicon tetrafluoride and found F = 19.09. Even if the method adopted by these investigators should be flawless it must not be forgotten that the figure for fluorine depends on the atomic weight of silicon, which was assumed to be 28.3. Any possible error in the latter value, it is true, would scarcely be sufficient to account for the high value for fluorine. It is safe to say, however, that the atomic weight of silicon is still too uncertain to serve for reference in fixing other atomic weights.

The paper by McAdam and Smith has already been mentioned. These authors converted weighed quantities of sodium fluoride into sodium chloride by means of hydrochloric acid gas, and from two analyses they derived two values for fluorine: 19.0176 and 19.0133 (with Na = 23.00 and Cl = 35.46). It may be gathered from their paper that the second conversion was possibly not quite complete. However, as the difference between these two values is very small it is permissible to take the average, or 19.015. This result is based on weighings in air. If the mean quantities involved be reduced to the vacuum standard and the atomic weight of fluorine be recalculated with the antecedents used in the present paper, F will be 19.009. This value agrees quite well with the value just found (19.005), particularly when it is realized that the method applied by McAdam and Smith would have a tendency to lead to a high value for fluorine. The sodium fluoride (produced by heating the acid salt) had to be used in a porous state and would have had a tendency to retain, or take up, a trace of water. (This was actually found not to be the case, however). The weight of the resulting sodium chloride, on the other hand, would have been too low if the conversion had not been quite complete. Either, or both, of these errors—if at all operative to a measurable degree—would have increased the value of the ratio NaF : NaCl, and hence the atomic weight of fluorine. For such reasons the agreement between McAdam and Smith's value (19.009) and that obtained in the present investigation (19.005) is all the more striking.

[14] In Abegg-Auerbach's Handbuch d. anorg. Chem., Vol. IV, part 2, p. 12 (1913).
[15] J. chim. phys. 11, 269–74 (1913).

CHAPTER III

REVIEW OF PREVIOUS DETERMINATIONS OF THE ATOMIC WEIGHT OF BORON.

GENERAL CONSIDERATIONS.

At this point it will be quite proper to consider the work of other chemists upon the atomic weight of boron and, if possible, point out the most probable errors which may have affected that work. It is not thought that the observations, and value for boron as given in this communication, are in any sense final, but great confidence is placed in them; and since this new figure for the atomic weight of boron is practically 1 per cent. lower than the constant now in use, this investigation would, indeed, be incomplete without a careful survey of previous determinations.

It is to previous analyses of borax that attention must be directed, for this compound of boron has been used extensively. It may be assumed that the preparations of borax used in such work in the past were of reasonable purity, the latter implying not merely the absence of appreciable traces of foreign matter, but also the proper proportion of the constituents of the salt itself. While, in some cases, exception to this assumption might be taken by the severe critic, it must be noted that many investigators do not describe the preparation of the borax used by them in sufficient detail to admit of a profitable criticism of the method of preparation.

In passing, it may be remarked that the analyses of boron compounds, other than borax, have not added materially to the existing knowledge of the atomic weight in question. Abrahall [1] determined the ratio $BBr_3 : 3Ag$, which (according to Clarke) leads to the value 10.819 for boron. The boron used in this preparation of boron tribromide had been obtained by the method of Wöhler and Deville and must have been rather impure. Gautier [2] analyzed the sulphide, carbide, chloride, and bromide of boron and obtained values the average of which is quite close to the

[1] Journ. Chem. Soc., **61**, 650 (1892). [2] Ann. chim. phys. (7) 18, 352 (1899).

number now in use, 11.0. It will be admitted, however, that the selection of the first two compounds (the sulphide and carbide) and the methods of analysis seem unfortunate for the purpose in view. Furthermore, Gautier himself admits [3] that the carbide was not pure.

The boron was prepared by Moissan's method and the sulphide, chloride, and bromide obtained from it were probably reasonably pure. Unfortunately, however, the methods of analysis are inadequate. The bromide of boron, for example, was analyzed as follows: The compound (on the average 3.5625 g. were used) was decomposed by water and the solution diluted to 1 liter. Portions of 50 c.c. each were withdrawn and the hydrobromic acid determined as silver bromide. The average quantity of boron tribromide actually analyzed, therefore, was only 0.1781 g.; the average amount of silver bromide actually determined weighed only 0.4002 g., not 20 times this amount. These figures (with Br = 79.92) would lead to 10.97 for the atomic weight of boron. This value, however, is rendered extremely uncertain by the volumetric operations and the author admits [4] that a variation of from 0.6 to 0.7 mg. ("at the most") in the weight of the silver bromide was considered satisfactory. A variation of $\pm$ 0.3 mg., would have caused the atomic weight of boron to vary from 10.78 to 11.16, whereas Gautier's own results vary only from 10.981

[3] The carbide of boron was heated in chlorine which removed the boron as BCl_3. The residual carbon was burned in oxygen and weighed as carbon dioxide. The accompanying two experiments are given by Gautier (loc. cit., p. 371). The author then continues as follows: "Le poids du carbone et celui de l'acide carbonique ne présentent pas une concordance absolue. Cela tient à la présence, dans le borure, d'une très petite quantité de matière étrangère; le poids de borure a été diminué de cette quantité pour le calcul." (!)

	B_6C	C	CO_2
(1)	0.2686	0.0429	0.1515
(2)	0.3268	0.0512	0.1844
	0.5954	0.0941	0.3359

The carbon corresponding to 0.3359 gram of CO_2 is only 0.0916 gram. The total amount of carbon actually found was 0.0941 g., or 0.0025 g. in excess of the theory. In other words, after removal of the boron as BCl_3, the total carbon left behind in two experiments contained 0.0025 g. (=2.66 per cent.) of an unknown impurity which was subtracted from the original weight of the boron carbide!

[4] "Pour déterminer la quantité d'acide bromhydrique contenu dans les solutions obtenues, nous avons fait chaque fois deux déterminations simultanées sur $\frac{1}{20}$ du volume total, soit sur 50 c.c., et nous n'avons considéré l'expérience comme valable que lorsque le poids de bromure d'argent obtenu pour chacune d'elles ne différait que de $\frac{6}{10}$ à $\frac{7}{10}$ de milligramme au plus." (Loc. cit., p. 377.)

to 11.043. Hence it must be inferred that the author rejected a number of analyses. The chloride was analyzed in a similar way.

These remarks suffice to indicate that the binary compounds of boron have not yet been analyzed with sufficient accuracy for atomic weight purposes. To this end a reinvestigation of the halides of boron would seem desirable and in such an investigation the more recent work of A. Stock et al.[5] might prove of great value, according to whom certain substituted hydrides of boron (*e.g.*, B_2H_5Br) must be regarded as analogues of the corresponding derivatives of carbon and hence seem to involve quadrivalent boron. On the other hand, boron appears to be strictly trivalent

TABLE 4.—*The atomic weight of boron derived from previous analyses of borax.*

	Year.	Atomic weight of boron as recalculated by—	
		Clarke.	Brauner.
(*a*) Determination of water in crystallized borax:			
Berzelius [1]	1822	11.019	11.08
Laurent [2]	1849		10.85
Dobrovolsky [3]	1869	10.855 11.532	10.87
Abrahall [4]	1892	10.702	10.70
Ramsay and Aston [5]	1893	10.942	10.94
Armitage [6]	1898	10.983	10.99
(*b*) The analysis of anhydrous borax (distillation method):			
Ramsay and Aston: [5]			
$Na_2B_4O_7 : 2NaCl$	1893	10.957	10.97
$Na_2B_4O_7 : 2NaCl : 2AgCl$ [5]	1893	11.054	11.05
(*c*) The titration of borax:			
Rimbach: [7]			
$Na_2B_4O_7.10H_2O : 2HCl$	1893	10.970 [8]	11.01 [8]
Armitage: [6]			
$Na_2B_4O_7 : SO_4$	1898	10.943	10.94

[1] Pogg. Ann. **2**, 129, **8**, 19.
[2] Compt. rend. **29**, 5.
[3] Quoted by Brauner in Abegg's "Handbuch, etc.," Vol. III, 1, p. 6 (1906).
[4] Jour. Chem. Soc. **61**, 650–666 (1892), (edited by Ewan and Hartog.)
[5] Ibid. **63**, 211–217 (1893).
[6] Chem. N. **77**, 78 (1898); see also Brauner, op. cit., p. 8, 9.
[7] Ber. **26**, 164–171 (1893).
[8] See note on p. 59

[5] A. Stock and O. Priess, Ber. **47**, 3109–13 (1914), and a number of other papers; see also reference on p. iii.

with reference to oxygen and the halogens. The tribromide, for example, was found to be incapable of combining with more bromine either at room temperature or at $-80°$.

It may be added, however, that the ratios $BX_3 : 3AgX$ and $BX_3 : 3Ag$ (X = halogen) are not particularly advantageous, for practical reasons. As already indicated by the editors of Abrahall's paper, an experimental error in the ratio $BBr_3 : 3Ag$ would be magnified 23 times in the atomic weight of boron.

In considering former analyses of borax itself, they may conveniently be discussed under three heads, as indicated in table 4. The last two columns give the atomic weight of boron as recalculated by Clarke and by Brauner, respectively.

A. The Determination of Water in Crystallized Borax.

It is generally conceded that the determination of water of crystallization in a salt is liable to lead to a doubtful atomic weight, since the water-content may vary with atmospheric conditions and since the salt may occlude traces of mother liquor. These objections, no doubt, also apply to crystallized borax; at the same time the dehydration of this salt seems to present even more serious difficulties which were overlooked or, at any rate, not fully appreciated by previous investigators; namely, the volatility of the borate itself and the retention of water by the end-product. The former was noticed, although underrated, by Abrahall and by Armitage; the latter, *i.e.*, the retention of water, it would seem, was first suspected, but not remedied, by Dobrovolsky.

These difficulties, particularly the retention of water, have been dwelt upon in the experimental part of the present work, but on account of their importance will bear repetition. It is evident from the earlier discussion of this question that borax can not be dehydrated quantitatively by ignition in an open vessel, such as a dish or a crucible, for the experimenter then faces the dilemma of either not removing the water completely or, if successful in this, of volatilizing some of the borax itself. In this connection Abrahall's own words may be of interest. He says:

"The determination of the atomic weight of boron by this method necessitates the determination of the precise range of temperature

[illegible] ... It must be inferred that the author rejected a number of [illegible]. The chloride was analyzed in a similar way.

These [illegible] indicate that the binary compounds of boron have not been analyzed with sufficient accuracy for atomic weight purposes. To this end a reinvestigation of the halides of boron [illegible] and in such an investigation the recent [illegible] of E. Stock et al.[1] might prove of great value, permitting [illegible] certain volatilizable hydrides of boron [illegible] to be regarded as analogues of the corresponding derivatives of [illegible] and hence using for [illegible] quadrivalent boron. On the other hand, boron appears to be directly trivalent

Table 4.—The atomic weight of boron derived from previous analyses of boron

	Date.	Atomic weight of boron as recalculated by—	
		Clarke.	Brauner.
(a) [illegible]	[illegible]	11.019	11.08
	[illegible]		10.85
	[illegible]	10.855	10.87
	[illegible]	11.022	
	[illegible]	10.792	10.70
	[illegible]	10.942	10.94
	[illegible]	10.893	10.99
(b) The analysis of [illegible]			
	[illegible]	10.867	10.97
	[illegible]	11.004	11.05
(c) The analysis of [illegible]			
	[illegible]	10.870	11.01
	[illegible]	10.843	10.94

[1] [illegible] 88, 253-257 (1915).
[2] [illegible] 38, 77-78 (1916); see also Brauner, [illegible] 38, 3-9, 9
[3] [illegible] 28, 164-171 (1902).
[4] See [illegible] 39

[1] A. Stock and O. Priedrici, [illegible] 54, 3229-32 (1921).
[illegible] reference on p. [illegible]

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s:

boro[illegible] hod
ran[illegible] ature

borax the atomic weight of boron may be calculated from the expression:

$$M = \frac{286.674 \times 70.546,}{100} \text{ or } B = 11.061 \quad . \quad . \quad . \quad (II)$$

These two results differ by 0.11, or fully 1 per cent., an error which can not be accounted for entirely by the solubility of silver chloride or the non-observance of the modern precautions in this precipitation.[8] Nor can it be due to residual boric acid in the sodium chloride, for the method pursued by those authors does not differ radically from that used in the present communication and, as carried out by them, may safely be assumed to lead to a quantitative elimination of the boric acid.[9] In fact, such errors as these, although probably not entirely absent, may be disregarded for the present. It is the gross errors, errors of the first magnitude, which should be ferreted out first. For similar reasons the etching of the glass vessel (mentioned by Ramsay and Aston), though by no means negligible, need not be considered. It is safe to assume that the silver chloride (which was collected in a Gooch crucible and finally dried at 200°) was determined with a tolerable degree of accuracy. If this be granted we shall be enabled to dispel the mystery surrounding the above inconsistent values.

It has been observed that fused borax, as prepared by Ramsay and Aston, invariably retains water. They had what, for the sake of convenience, has in this paper been termed "borax glass," *i.e.*, vitreous borax, insufficiently fluxed for the complete removal of water. This point should be stated with emphasis. The sodium

[8] The present writers do not underrate the importance, in such work, of the solubility of silver chloride. However, it is highly probable that Ramsay and Aston worked with too concentrated solutions, and under such conditions silver chloride invariably occludes appreciable quantities of other salts (see Richards and Wells, Carnegie Inst. Washington, Pub. No. 28, p. 31 et seq.). In other words, these two errors would have balanced each other, to some extent at least. In view of the much more serious and obvious errors, soon to be discussed, it seems permissible to assume that the solubility of silver chloride in Ramsay and Aston's work is *relatively* unimportant.

[9] According to our interpretation, Ramsay and Aston do not "admit" (see Brauner's criticism in Abegg's Handbuch III (1), p. 7 (1906)), that the conversion of borax into sodium chloride was incomplete, but merely consider it as a contingency, as "not improbable," in their own words, solely in an attempt to account for the discrepancy between the two results derived from the ratios $Na_2B_4O_7 : 2NaCl$ and $Na_2B_4O_7 : 2AgCl$, respectively.

chloride obtained was finally dried at about 350° in a current of air and, therefore, must also have retained some moisture, for sodium chloride, as obtained under the conditions of the experiment must be *fused* for the complete expulsion of the last traces of water.[10] It is practically certain, therefore, that these two sources of error were operative; doubt can be entertained only concerning their magnitude. Fortunately the determination of the latter is not entirely beyond our reach.

Again, the residual water in fused borax, as prepared by Ramsay and Aston, is fairly constant and amounts to about 0.2 per cent. It is highly probable that the percentage of water in the "borax glass" used by those investigators was even greater, for the low density of their vitreous borax (2.29, as against the more probable value 2.357; see p. 24) is probably not without significance and may be taken to show that their "borax glass" was not entirely free from flaws which, in this case, are not only due to air, but to a mixture of the latter with steam. It may be quite reasonably assumed that this borax glass contained approximately 0.3 per cent. of water. It now remains to be seen whether we can also arrive at some legitimate estimate concerning the amount of moisture in the sodium chloride. This, the writers hope, can also be done, with a fair degree of certainty, without drawing upon the imagination.

From Ramsay and Aston's work the ratio AgCl : NaCl may be computed. The same ratio has been determined, much more accurately, by Richards and Wells. The two ratios, as given by Clarke, are as follows:

$$\frac{100\ \text{NaCl}}{\text{AgCl}} = 40.867 \text{ (Ramsay and Aston)}$$

$$\frac{100\ \text{NaCl}}{\text{AgCl}} = 40.7797 \text{ (Richards and Wells)}$$

[10] Sodium chloride is particularly prone to retain traces of water or mother liquor when crystallized from water solution. It seems safe to say that sodium chloride, prepared in this manner, that does not slightly decrepitate just before fusion is yet to be made. In their work upon the atomic weight of columbium (J. Am. Chem. Soc. 37, 1783 (1915)) the writers found that sodium chloride dried at about 400° was not free from water. In some cases it retained over 0.1 per cent. of moisture which was not given off until the salt was fused. (This statement, although not recorded in the paper just mentioned, is borne out by original notes.)

As already intimated, this difference is probably very largely due to moisture in the sodium salt. If the discrepancy be *entirely* due to this cause the amount of moisture may be computed from the ratios. It will be found that the moisture in Ramsay and Aston's sodium chloride *may* have amounted to 0.214 per cent. One will not go far wrong, therefore, by assuming that the sodium chloride contained approximately 0.2 per cent. of water. This amount may seem high, but is not beyond the range of possibility.[11]

On now applying these corrections, approximations though they be, to expressions (I) and (II) there would result:

$$M = \frac{116.908 \times (100 - 0.3 \text{ per cent.})}{57.933 - 0.2 \text{ per cent.}} \quad \text{or } B = 10.901 \quad . \quad . \quad . \quad . \quad (I_A)$$

$$M = \frac{286.674 \times (70.546 - 0.3 \text{ per cent.})}{100} \quad \text{or } B = 10.909 \quad . \quad . \quad (II_B)$$

These corrections, far from arbitrary, not only harmonize the inconsistent results obtained by Ramsay and Aston, but lead to values which corroborate the figure found in the present investigation (10.900). The agreement thus established is striking.

The argument may be supported in still another manner, as follows: If Ramsay and Aston's weight of their "anhydrous" borax be allowed to stand as recorded by them and the hypothetical correction (-0.2 per cent. H_2O) be applied only to their sodium chloride there would follow:

$$M = \frac{116.908 \times 100}{57.933 - 0.2 \text{ per cent.}} \quad \text{or } B = 11.052 \quad . \quad . \quad (I_B)$$

It has been shown (see p. 43) that if such insufficiently dried borax and a water-free end-product had been used in the calculations the result for boron would have been 10.999. In this case the "borax glass" would have contained approximately 0.2 per cent. of water. In the last column in table 2 it has also been shown that if our own borax glass, other things being equal, had contained as much as 0.3 per cent. of moisture (the amount probably

[11] See preceding note. In the present case part of this moisture may have been held in combination with the trace of silica resulting from the etching of the glass vessel, for drying at 350° would not have been sufficient to completely dehydrate silicic acid.

contained in Ramsay and Aston's material) the atomic weight of boron would have become 11.052. This figure is identical with the value just derived above (Ib), upon the same assumption, from Ramsay and Aston's work. It is, furthermore, of the same order of magnitude as that calculated in expression (II), which gave B = 11.061 and, according to argument, also involved borax containing 0.3 per cent. of water and a water-free end-product (in this case silver chloride). True, these values of 11.05, or thereabouts, are incorrect. Nevertheless their concordance with each other appears to furnish additional, though indirect, proof of the essential correctness of our original assumptions.

This completes the argument concerning Ramsay and Aston's work. The reasoning seems conclusive and completely deprives Ramsay and Aston's results of incongruities which would scarcely yield as plausibly to any other theories or assumptions. True enough, the quantities of moisture called for by our explanation seem unusually large, not to say excessive. These quantities, however, have been shown not to exceed reasonable limits in this particular case. That the worker in atomic weights must ever be on guard against traces of water in the substances which go to make up the ratio sought has been pointed out repeatedly, and with emphasis, by T. W. Richards. The present case seems to be an unusually forceful illustration of this contention. The percentages of moisture involved in this instance are not merely traces, but quantities which should not be neglected in a careful every-day analysis. We should probably search the entire field of atomic weight determinations in vain for another case so obstinate in this respect and so disastrous in its effect as that presented by borax.

These remarks, of course, are not meant to suggest that the corrections for moisture should be applied to Ramsay and Aston's results for practical ends; they are too hypothetical for a rigid computative revision. However, the corrections are far from arbitrary and, if applied only for the sake of argument, not only dispose of a grave and puzzling inconsistency, but also lead to values practically identical with the one found in the present investigation. Such considerations seem to offer an acceptable excuse for the digression.

C. The Titration of Borax.

Rimbach dissolved known quantities of crystallized borax in water and titrated the solution, using a weight-burette, with dilute hydrochloric acid which had been standardized by precipitation with silver nitrate. The percentage of actual hydrogen chloride was computed from the total silver chloride obtained in three independent determinations. Methyl orange, said to be indifferent to boric acid, was used as an indicator. With the atomic weights which (in 1893) seemed most reliable to him, Rimbach himself derived the value 10.945 for the atomic weight of boron. Subsequent recalculations of his analyses point to a much higher figure, that is to say, to the value now in use, 11.0. It was not until the present investigation had practically been completed that it was thought desirable to recalculate Rimbach's analyses with the atomic weights used in the derivation of our own value for boron. The figure thus found was 10.917.[12] That, for present purposes, Rimbach should be credited with the latter value is permissible. It thus appeared, quite unexpectedly, that this recalculated value (10.917) agreed more closely with our own (10.900) than any other previous determination.

Although Rimbach's value, as recalculated by the writers, is probably nearer the true atomic weight of boron than that found by any of his predecessors in this field, the methods pursued by him are open to a number of objections. We shall not dwell upon those of a more general character: That a titration method, in general, is inferior to a purely gravimetric method; that the use of a hydrated salt is not advisable; or that the hydrochloric acid might have been standardized, preferably, by a method involving the use of the indicator to be used in the final titrations. The chief errors which may have crept into Rimbach's work are of a more serious nature and deserve attention here.

In order to free borax from adherent moisture, Rimbach exposed the finely powdered decahydrate to the air, merely pro-

[12] Rimbach, using the older atomic weights, finds his hydrochloric acid to contain 1.84983 per cent. of actual hydrogen chloride. This percentage has been retained, inadvertently it would seem, both by Clarke and by Brauner. The present writers, using the newer atomic weights, obtained 1.85095 for the percentage strength of Rimbach's acid. With this figure, and from the mean quantities involved in the final titrations, the atomic weight of boron was computed and found to be 10.917. The calculation was based on the atomic weights used in the present work and, in addition, on H=1.0076 and Ag=107.880.

tecting it from dust. The salt, stirred frequently, was thus exposed for 12 days, by the end of which period the weight had become practically constant. It was then assumed to have the theoretical composition of the decahydrate.

When carbon dioxide is passed through a solution of borax a partial decomposition into sodium carbonate and boric acid takes place; a solution thus treated will finally effervesce upon the addition of an acid. It is only reasonable to suppose, therefore, that the moist borax crystals would also absorb some carbon dioxide from the air. Such an absorption might take place, of course, simultaneously with the evaporation of moisture, so that the net result might still be a decrease in weight. In fact, it was found that a sample of moist, powdered borax, entirely free from carbonate, after being exposed to the laboratory air for several weeks, gave a very slight effervescence with dilute hydrochloric acid. The reaction was slight, but unmistakable. This action of carbon dioxide on the moist crystals probably becomes inappreciable as soon as the borax is "air-dry." To what extent carbon dioxide may have affected Rimbach's salt it is impossible to say. The effect may have been negligible. Nevertheless the fact remains that no steps were taken to eliminate this source of error, however slight it may have been. The question is of much interest for another reason. As borax, contaminated with traces of carbonate, is said to effloresce more readily than the pure salt, any absorption of carbon dioxide even might have been accompanied by a slight loss of water of crystallization itself.

While the influence of the factors just discussed is rather uncertain, an error which may have affected the final titration is much more tangible and must not be dismissed without comment. In the titration of borax it is assumed that the boric acid resulting from the reaction has no effect upon methyl orange. This assumption, the writers believe, is not strictly correct, for according to their experiments solutions of pure boric acid, particularly when fairly concentrated, are distinctly acid toward this indicator, and it is only in every-day analytical work that this factor may safely be neglected; not so, it would seem, in an analysis of precision. Rimbach, it is true, did not neglect to carefully consider this very point. He found, from a series of experiments, that a solution containing 9 grams of pure ortho-

boric acid and 5 grams of pure, neutral sodium chloride, and an equal volume of pure water—both liquids containing the same amount of the indicator—required practically equal amounts of dilute hydrochloric acid for the production of the same tint. He naturally concluded from these results that boric acid was neutral to the indicator. It should be remembered, however, that Rimbach's hydrochloric acid was approximately half-normal; for he distinctly states that this acid was used in these tests. Now, an acid of this concentration is not sufficiently dilute to detect, with certainty, any slight difference in reaction between the two solutions, that is to say, between the boric acid solution and the "blank." This may be gathered from the following simple experiment:

A beaker contained a solution of 9.7 grams of pure H_3BO_3 in 450 cubic centimeters of distilled water. This approaches the quantity and concentration of the boric acid produced in the titration of about 15 grams of crystallized borax, the largest single portion used by Rimbach. A similar beaker contained the same volume of distilled water which came from the same source and the same container as that used in the first beaker. Ten cubic centimeters[13] of a methyl-orange solution, containing 0.010 gram of the dye per liter, were added to the contents of each beaker. The tints produced in the two vessels, when viewed separately, indicated neutrality or, possibly, a slight alkalinity in each case. When the boric acid solution and the blank were placed side by side, however, a distinct difference was noticeable: The boric acid solution was slightly acid with reference to the blank. In fact, this difference could easily be measured. The water containing only the indicator required the addition of 0.5 c.c. of $\frac{N}{20}$ hydrochloric acid solution. It will be observed that this hydrochloric acid is much more dilute than that used by Rimbach in a similar test. A second experiment involving the same quantities gave like results. Finally 5 grams of pure sodium chloride were dissolved in the solution containing the boric acid; a change in color was not to be observed, which shows that the sodium chloride, produced in the titration of borax, does not perceptibly

[13] Contrary to what might be expected, this amount gives only a faint color under the conditions and probably represents a practicable minimum. The indicator was prepared and used as directed by Rimbach.

affect the end-point. Furthermore, these experiments prove that boric acid does influence the end-point, inasmuch as the latter is reached prematurely, that is to say, before it would be reached if no boric acid were present.

In order to fix the end-point with precision Rimbach, in the final titrations, proceeded as follows: Standard hydrochloric acid (about $\frac{N}{2}$) was added to the borax solution until a faint acidity was indicated. A more dilute acid (about $\frac{N}{6}$) was then added to a blank until the tint was exactly equal to that of the former solution. The more dilute acid thus required—expressed in terms of the original standard—was subtracted from the acid added to the borax solution and the difference was taken to represent the hydrochloric acid actually needed to react with the borax. It is evident that this mode of procedure did not correct for any possible acidity of the boric acid itself; and if our observations in regard to the acidity of this acid be correct, it is also certain that the approach of the end-point was thus hastened somewhat and that, therefore, the amount of hydrochloric acid recorded was slightly insufficient.

Obviously we are now in a position to apply a correction to Rimbach's results. But as the concentration of the borax solutions used by him and, hence, that of the boric acid solution formed, can only be reproduced approximately, such a correction for the acidity of boric acid can not be rigidly applied. Furthermore, the standard of the acid used by the writers to measure this acidity was not determined with the idea of actually revising Rimbach's results on this basis. Nevertheless it may be of interest to see how and to what extent such a correction would have influenced Rimbach's value for boron. If, from the above data, we calculate the value of this correction for the mean quantity of borax titrated by Rimbach, the atomic weight of boron would be lowered from 10.917 to 10.887. It is thus seen that a slight inaccuracy in the method, an inaccuracy which would not be noticeable in ordinary analytical work,[14] would affect the atomic weight of boron to the extent of nearly 0.3 per cent. of its approximate value!

[14] In the titration of 1 gram of crystallized borax this error due to the acidity of boric acid would be equivalent to less than 0.02 c.c. of $\frac{N}{10}$ hydrochloric acid, an entirely negligible amount.

To summarize regarding Rimbach's determination: The main factors to be considered in his work are the following: Absorption of carbon dioxide by the borax; improper water-content of the salt; and a slight acidity of boric acid toward the indicator. As no definite conclusions can be reached as to the extent, if any, of the first two factors, it is not possible to say whether Rimbach's result may be high or low. Any errors due to the standardization of the hydrochloric acid, by means of silver chloride, are probably of a different order and of smaller significance than those just mentioned. At any rate, it is interesting that Rimbach's result (10.917, as recalculated by the writers) agrees tolerably well with the value (10.900) found in the present investigation.

The above test for the slight acidity of boric acid toward methyl orange would, of course, be utterly useless if the boric acid were contaminated by traces of other acids, such as sulphuric acid. Unfortunately the acid prepared from methyl borate had all been used in the preparation of borax; hence, for the above tests the boric acid was prepared as follows: A good commercial grade of boric acid (which did contain a bare trace of sulphuric acid) was twice recrystallized from water. It was then fused in a platinum dish and recrystallized once more from pure water. The product was again dissolved in boiling water and, after complete solution, a few cubic centimeters of redistilled ammonium hydroxide were added. The mother liquor from the crystals of boric acid separating out from this solution was strongly alkaline to methyl orange, due to the formation of some ammonium borate. The boric acid thus obtained was recrystallized four times from water. Centrifugal draining and washing were resorted to throughout. The final product, in concentrated solution, was again distinctly acid to methyl orange. It seems unlikely that this acidity was due to anything but the boric acid itself. This preparation was used in the quantitative tests.

An exhaustive study of the accurate titration of borax was not considered to be within the scope of the present paper.[15]

The two titrations of borax carried out by Armitage do not require a lengthy discussion. This investigator modified Rimbach's method by substituting fused borax (supposedly anhy-

[15] It may be added that according to Joly (Compt. rend. **100**, 103, 1885) solutions of boric acid, dilute or concentrated, are neutral to methyl orange.

drous) for the decahydrate and by using dilute sulphuric acid instead of hydrochloric acid in the titration. His determinations, which were probably largely preliminary in character, have been published only in abstract. The experimental data on the titration of borax—privately communicated to Brauner [16] upon the latter's request—are not sufficient for a complete recalculation.

In the abstract read before the Chemical Society it is stated:

"A given weight of fused borax was dissolved in water and titrated with dilute sulphuric acid, the strength of which had been determined (I) by titration with solution of pure soda of known strength, (II) as barium sulphate. The value 10.928 was obtained for the atomic weight of boron as a mean of two experiments performed by this method." [17]

The quantities of SO_4, given by Brauner, equivalent to the portions of borax used are probably the values *calculated* by Armitage himself. The experimental data upon which these calculations were based (weight of $BaSO_4$, etc.) have not been published.

SUMMARY.

The results and conclusions arrived at in the preceding investigation may be summarized as follows:

(1) Anhydrous sodium tetraborate, by treatment with appropriate acids and by repeated evaporation with methyl alcohol, was converted, both directly and indirectly, into the chloride, fluoride, sulphate, nitrate, and carbonate of sodium.

(2) The borax used for this purpose was prepared by synthesis from pure sodium carbonate and boric acid. The latter had been obtained by the saponification of distilled methyl borate.

(3) The complete dehydration of borax was found to be quite difficult and could be effected only by prolonged fusion. "Borax glass," as obtained ordinarily, was found to hold about 0.2 per cent. of water. The complete removal of the latter, without loss of borax by volatilization, was probably effected for the first time and, of course, was of the utmost importance in an investigation of this kind. The difficulty encountered in the complete dehydration

[16] Op. cit., p. 9.

[17] Chem. N. 77, 78 (1898).

of borax has been discussed in detail and—rightly or wrongly—has been attributed to a transient hydrolysis in the earlier stages of the dehydration.

(4) The removal of boric acid by the method indicated under (1) proved to be complete and left little to be desired. The methyl alcohol used for this purpose was prepared by the saponification of distilled methyl oxalate. The essential factors in the volatilization of boric acid seem to be the following:

(*a*) Both the residue treated and the pure methyl alcohol used should be as free from water as possible, if the elimination of the boric acid is to be effected with a minimum of alcohol.

(*b*) Frequent evaporations to dryness with small quantities of methyl alcohol, particularly toward the end of the process, are preferable to fewer evaporations with larger quantities.

(*c*) Two or three consecutive evaporations with methyl alcohol should, preferably, be followed by solution of the residue in water and evaporation to dryness. Toward the end of the process these evaporations, with alcohol and water, may be alternated to advantage.

Incidentally, it is safe to assert that, if these precautions be observed in the estimation of boric acid in a soluble borate by the Gooch-Rosenbladt method, any lack of success is to be attributed to the "retainer" used for fixing the boric acid—in short, to what is taking place in the receiver, not to incomplete volatilization of the boric acid.

(5) The direct conversion of borax into sodium fluoride (*i.e.*, in the presence of hydrofluoric acid) was found to be impracticable and was brought about indirectly through the formate; the latter, after removal of the boric acid, being easily transposed by hydrofluoric acid. The advantages of formic acid for this particular purpose have been given.

(6) The atomic weight of boron was not derived from a series of identical conversions of borax into some fixed salt, but was based on the equivalent quantities of a number of different sodium salts, such as the chloride, sulphate,

nitrate, and carbonate. The value of such a method is obvious. The atomic weight of boron thus found was **10.900,** referred to the oxygen standard.

(7) These data, which included the ratio between sodium tetraborate and sodium fluoride, were also used for a recalculation of the atomic weight of fluorine which was thus found to be **19.005.**

(8) The new value for boron (10.900) is practically a whole per cent. lower than the one at present in use (11.0). It seemed desirable, therefore, to search for the chief cause, or causes, of this discrepancy. As the writers are not aware of any serious flaws in their own determinations, it became imperative to subject the work of others to a somewhat critical study. A number of palpable errors in such work have been pointed out, chief among which is the retention of water by "borax glass." In the light of this criticism of previous determinations it would seem that the various sources of error had conspired, as it were, in favor of the higher value (11.0) for boron. The evidence, both direct and inferential, collected in Chapter III in support of the lower figure (10.900) seems little short of conclusive.

(9) It is of particular interest to note that if the present writers had used incompletely dehydrated borax—as was done in the past—the atomic weight of boron would have been 11.0. This result, though incorrect, is of value in clinching the argument in favor of the new value (10.900).

(10) It should be borne in mind that the present work, including the discussion of previous determinations, was confined to borax. It has been hinted, however, that the analyses of other compounds of boron, recorded in the literature, also lead to rather uncertain values for boron. A careful analysis of such compounds, particularly of the halides, would be of interest and furnish a valuable check upon the value derived in the present study.

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